Utilization of Industrial Wastes and Waste By-Products for Phosphorus Removal An Inventory and Assessment Research Report No.6

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Research Program for the Abatement of Municipal Pollution under Provisions of the Canada-Ontario Agreement on Great Lakes Water Quality

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Utilization of industrial wastes and waste by-products for phosphorus removal : an inventory and assessment /

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UTILIZATION OF INDUSTRIAL WASTES AND WASTE BY-PRODUCTS FOR PHOSPHORUS REMOVAL: AN INVENTORY AND ASSESSMENT

by

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ABSTRACT

In this study, 141 Ontario and Quebec companies were contacted regarding waste products with potential utility for phosphorus removal. An inventory of waste products was compiled and several different types of waste material produced by 48 separate companies were evaluated for phosphorus removal efficiency by jar testing procedures. Several wastes with varying degrees of usefulness were identified -- i.e., pickle liquors, reclaimed $FeSO_4.7H_2O$, mill scale, spent mine acid, carbide lime, stack precipitator dusts, dross, red mud, and certain bag-house dusts and slags. The problems associated with using the various waste materials were discussed and estimates made of the quantities available and the amount of wastewater that could be treated.

The effects of pickle liquor additions on a bench-scale activated sludge process were investigated. A dosage of pickle liquor at 20 mg/l as Fe gave effluent phosphorus levels consistently less than 1 mg/l for influent phosphorus levels varying as high as 9.3 mg/l. The pickle liquor did not affect COD removal efficiency, or cause significant changes in effluent pH or heavy metals content. Essentially all of the heavy metals added with the pickle liquor were accumulated in the mixed liquor solids.

Ferric sulphate $[Fe_2(SO_4)_3]$ produced from a sludge incinerator ash was evaluated for phosphorus removal on a pilot scale (20 Igpm). It was found that a dosage slightly in excess of 15 mg/l as Fe gave effluent

phosphorus levels less than 1 mg/l. Again, heavy metals added with the $Fe_2(SO_4)_3$ were accumulated in the sludge rather than carrying over in the effluent.

Full-scale phosphorus removal studies at a local wastewater treatment plant (Dunnville, Ontario) using pickle liquor were closely monitored with respect to heavy metals levels in the various plant streams. For all metals, with the exception of iron, there was no increase in metal transport through the plant in going from baseline to pickle liquor addition conditions. There were, however, significant increases in all metal concentrations in the mixed liquor, aerobic digester and waste sludge solids.

RÉSUMÉ

On a consulté 141 sociétés de l'Ontario et du Québec pour cette étude portant sur les déchets utilisables pour l'élimination du phosphore. À partir d'un inventaire des déchets industriels, on a évalué certains types de déchets produits par 48 sociétés différentes, au moyen de tests à l'éprouvette. C'est ainsi qu'on a identifié quelques déchets possédant un degré quelconque d'utilité, comme les solutions de décapage, $FeSO_4 \cdot 7H_2O$ récupéré, les battitures l'acide résiduaire des mines, la chaux à teneur de carbure, les poussières des précipitateurs de cheminées, les scories, la boue rouge, la poussière et la crasse des installations de filtrage. On a discuté des problèmes qui pourraient être engendrés par l'utilisation des différentes sortes de déchets et on a cherché à en évaluer les quantités disponibles et le volume d'eaux usées qui pourrait être traitée.

On a étudié sur modèle réduit les effets produits par les solutions de décapage dans un procédé de traitement par boue activée. L'addition de décapant à une dose de 20 mg/l (de Fe) a donné comme concentration en phosphore de l'effluent des valeurs qui se situaient en dessous de 1 mg/l alors que la concentration de phosphore de l'affluent atteignait jusqu'à 9.3 mg/l. Ces eaux de décapage n'ont ni nui au bon fonctionnement de la suppression de la DCO ni fait varier de façon significative le pH ou la teneur en métaux lourds de l'effluent. De façon générale, tous les métaux lourds ajoutés en même temps que la solution de décapage se sont accumulés parmi les solides du mélange (liqueur mixte).

À l'échelle pilote (20 gal imp /mn), on a évalué l'élimination du phosphore par du sulfate ferrique ($Fe_2(SO_4)_3$) extrait des cendres de boues incinerées. On a ainsi découvert qu'une dose un peu supérieure à 15 mg/l de Fe a donné des concentrations en phosphore de l'effluent de moins de 1 mg/l. Encore une fois, les métaux lourds ajoutés en même temps que $Fe_2(SO_4)_3$ se sont fixés dans la boue au lieu de se déverser dans l'effluent.

Des études ont été effectuées à l'usine d'épuration d'eau de Dunnville, Ontario, sur l'élimination du phosphore, à l'aide de solutions de décapage et on a rigoureusement contrôlé la concentration de métaux lourds dans les différentes conduites de traitement de l'usine. Sauf dans le cas

du fer, le fait de passer du traitment normal à un traitement avec addition de décapant n'a entraîné aucune augmentation du transport des métaux à travers l'usine. Cependant, il y a augmentation significative de la concentration en métaux des solides de la liqueur mixte, du digesteur aérobique et des boues résiduaires.

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CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

In this investigation, a number of industrial waste products were inventoried and found to be applicable to the chemical precipitation of phosphorus from municipal wastewaters. The major conclusions of this phase were:

(i) pickle liquors from several steel companies, $FeSO_4.7H_2O$ reclaimed from pickle liquors by an acid recovery process and carbide lime from acetylene generation were capable of consistent phosphorus removal (< 1 mg/l) at doses comparable to the traditional commercial iron and lime coagulants;

(ii) a spent mine acid leach solution was useful for phosphorus removal but the excess acidity must be neutralized before or during use, or the iron content augmented by solubilizing additional iron with the excess free acid;

(iii) stack precipitator dusts, bag house dusts and red mud were capable of achieving phosphorus removal; however, they must be added at relatively large, impractical dosages and cause an inordinate increase in sludge volume;

(iv) the acid and alkali leachates of mill scales from steel production and forming and dross from aluminum smelting gave ferrous iron and aluminate solutions, respectively, that were capable

of efficient phosphorus removal.

Pickle liquor additions to a bench-scale activated sludge process were investigated and the following conclusions are appropriate:

(i) a pickle liquor dosage of 20 mg/l as Fe gave effluent phosphorus levels consistently less than 1 mg/l when influent phosphorus levels were less than 7 mg/l;

(ii) synthetic sewage studies with controlled influent phosphorus and pickle liquor levels indicated that there was a pseudo-stoichiometric relationship between influent phosphorus and the iron dosage required to reach a 1 mg/l effluent phosphorus;

(iii) pickle liquor additions at 20 mg/l as Fe caused a slight decrease in effluent pH of approximately 0.5 units;

(iv) pickle liquor additions did not affect the COD removal efficiency of the activated sludge process;

(v) heavy metals were added with the pickle liquor; however, these accumulated in the mixed liquor solids and were not transported with the effluent.

Pilot plant studies with a ferric sulphate produced from sludge incinerator ash treating a domestic wastewater showed that effluent phosphorus levels of less than 1 mg/l would be achieved at a dosage slightly in excess of 15 mg/l as Fe. Improvements in suspended solids and BOD removal efficiencies were also noted. Heavy metals added with the ferric sulphate accumulated in the primary sludge.

Full-scale pickle liquor studies at the Dunnville Wastewater Treatment Plant demonstrated that --

(i) pickle liquor additions at approximately 6 mg/l as Fe did not increase effluent metal levels, except for iron;

(ii) metals accumulated in the mixed liquor solids and were physically concentrated further in the aerobic digester and waste sludge solids;

(iii) the metals did not appear to resolubilize in the aerobic digestion process or during lagooning as evidenced from the low metal levels in the digester and lagoon supernatant return streams.

RECOMMENDATIONS

The main recommendations arising from this study are as follows:

(i) in order to reduce costs, full utilization, wherever possible, should be made of waste pickle liquors, $FeSO_4.7H_2O$ and carbide limes for phosphorus removal;

(ii) further studies (It is noted that studies are presently underway on land disposal of chemical sludges.) should be carried out to determine the environmental impact of disposing of high metal content waste sludges from pickle liquor phosphorus

removal systems;

(iii) further feasibility and economic investigations should be conducted on producing low-cost iron salts from waste sources such as mill scales and aluminate from dross. This aspect has been dealt with in part in a separate, but related, report by Scott (1973).

CHAPTER 1

BACKGROUND AND STUDY OBJECTIVES

1.1 BACKGROUND

The removal of phosphorus from municipal wastewaters is presently considered essential to reducing the eutrophication potential of these effluents on receiving waters. Chemical precipitation of phosphorus compounds by the use of lime, iron or aluminum salts is regarded by Jones (1972), Jenkins et al (1971) and others as the most economical means of effecting this removal and has been the subject of numerous studies.

The implementation of the Canada/Ontario Agreement for Great Lakes Water Quality [see Prince and Bruce (1972) for details] has necessitated phosphorus removal at all municipal wastewater treatment facilities in the Lake Erie watershed by 1974 and in the Lake Ontario watershed by 1976. This widespread phosphorus removal program in the Lower Great Lakes will create a significant demand for the traditional (alum, lime and ferric chloride) chemical precipitants. Because of the cost and occasional limited availability of these chemicals, alternate precipitant sources have also been investigated. For example, in Ontario, waste pickling liquors from steel mill operations have been used at Chatham and Dunnville in controlled dosages to remove phosphorus from the municipal wastewaters. The advantages of using a waste product for

phosphorus removal are two-fold in that it provides a minimal cost precipitant while at least partially solving the particular industry's waste disposal problem.

Industrial waste utilization experiments have generally met with some measure of success; however, a limited number of studies have investigated the possible undesirable side effects caused by the impurities in the waste. For example, the Sewerage Commission of the City of Milwaukee (1971) found that an average pickle liquor dose of 9.4 mg/l as Fe to the wastewater caused no reduction in the BOD removal efficiency, nor did it adversely affect the mixed liquor biota. The 2.1 to 9.3% free sulphuric acid content of the pickle liquor caused a nominal decrease in effluent pH from 7.1 to 7.0; however, the fate of potentially toxic heavy metals in the pickle liquor was not investigated.

Cousins (1960) reports that metal ions in low concentrations are tolerable by bacteria but may become inhibitory at higher concentrations. Both aerobic and anaerobic bacterial species can become acclimatized to such ions. Jenkins and Hewitt (1942) found that 5 mg/l Cr^{6+} in the sewage stopped all nitrification in activated sludge, but that 2 mg/l Cr^{6+} only partially inhibited nitrification. Increased complexing of the metals by such ligands as nitrilotriacetic acid (NTA) may reduce their toxicity by lowering the concentration of free metal available to interact with the biota.

Abbott (1971) has noted that many metals tend to concentrate in the digester sludges. Although plant influent levels may be in the

microgram to low milligram per litre range, digester contents can approach several hundred mg/l. The actual levels of metal ions are, of course, quite variable and depend on the nature of the wastewater and the treatment process.

Bjorndal et al (1972) found that certain metal ions, such as nickel, when complexed by such species as NTA, tend to remain soluble throughout the treatment process and carry over in the effluent. Other metals, such as copper and cadmium, are largely adsorbed on the biological flocs and are removed with the waste sludge. Consequently, the possibility exists for significant heavy metal transport through treatment plants when wastewater NTA levels are high (i.e., a detergent reformulation situation) and when chemical phosphorus removal with a pickle liquor is being practised.

1.2 STUDY OBJECTIVES

This study was designed to investigate alternate precipitant sources, such as industrial wastes and waste by-products, which may have application in phosphorus removal. Particular emphasis was placed on the phosphorus removal capability of the materials and on ascertaining any complications associated with their use. Individual objectives of the study were as follows:

(i) to compile an inventory of potentially useful waste sources as to the nature of the waste, location and quantity produced;

(ii) to assess the wastes as to composition, phosphorus removal capabilities (dose and optimum pH) and to determine any side effects

associated with their use;

(iii) to determine, using bench-scale continuous flow reactors, the effects of direct pickle liquor additions on the activated sludge process with respect to removal efficiencies, effluent heavy metal carry-over, etc.;

(iv) to determine on a pilot scale the phosphorus removal efficiency and associated side effects of liquid ferric sulfate precipitant produced from sludge incinerator ash;

(v) to conduct full-scale studies on an activated sludge plant receiving pickle liquor additions to determine the fate of selected heavy metals in the treatment process.

A separate report closely related to this investigation, by Scott (1973), deals with the economic aspects of utilizing certain industrial wastes or reprocessed waste products for phosphorus removal.

CHAPTER 2

INVENTORY AND EXPERIMENTAL PROCEDURES

2.1 INVENTORY PROCEDURE

The companies contacted about waste products were intentionally limited to Ontario and Quebec, since this region is closest to the Lower Great Lakes -- the area of greatest current demand for precipitants. A list of potential companies (see Appendix A) was extracted from trade directories. [Fraser's Canadian Trade Directory (1972) and Canadian Trade Index (1971)]. Potential companies were those utilizing iron, aluminum and lime, and which were found under such headings as alloys, aluminum, anodes, automobiles, calcium, cement, iron, manufacturing, mining, plating, screws, steel, tanks, tubes, wire, etc.. An additional information source was provided by the Ontario Water Resources Commission (presently, Ministry of the Environment) Survey Series, which details the effluents of companies operating in various counties of Ontario.

Each company was contacted (see letter format in Appendix A) explaining the nature of the study and requesting appropriate samples for evaluation. Any response from the company was pursued and shipping of the samples was arranged.

2.2 PRELIMINARY ASSESSMENT PROCEDURES

The phosphorus removal capability of all waste samples was assessed using standard jar testing procedures. The format for a particular jar test was as follows:

(i) a grab sample of degritted raw sewage from the Burlington Skyway Treatment Plant was collected and divided into six one-litre aliquots;

(ii) the material to be tested was added in varying concentrations (e.g. -- 0, 5, 10, 15, 20 and 30 mg/l);

(iii) the mixture was flash mixed for 5 minutes at 100 rpm;

(iv) flocculated for 10 minutes at 40 rpm;

(v) slowly stirred for 90 minutes at 10-15 rpm;

(vi) quiescently settled for 10 minutes;

(vii) a supernatant sample was then decanted for a total unfiltered phosphorus determination;

(viii) the final supernatant pH was determined.

Any pH adjustments were made by adding 10 N H_2SO_4 or 10 N NaOH to the sample during the initial flash mixing step. The analytical procedures are outlined in Appendix C.

This jar testing procedure was replicated two to four times for each waste product to determine the dosage required to attain a 1 mg/l phosphorus concentration in the effluent and the optimum pH for phosphorus removal. The results for various types of waste are summarized in Chapter 3.

2.3 PROCEDURE FOR EVALUATING EFFECTS OF PICKLE LIQUOR ON AN ACTIVATED SLUDGE PROCESS

Two continuous laboratory scale activated sludge units were constructed to operate in parallel. Pickle liquor was added continuously to the aeration tank of one unit, while the other unit served as a control.

A schematic diagram of the unit appears in Figure 1.

The units were fed in parallel at identical rates using degritted raw sewage from the Burlington Skyway Treatment Plant. The flow rate to each was 50 ml/min during the day and 30 ml/min at night, giving respective retention times of 3.0 and 5.0 hours in the nine-litre aeration tanks and 1.2 and 2.0 hours in the 3.8-litre clarifiers.

A typical pickle liquor was used for the duration of the experiment. Its average composition was 60 g/l Fe, 116 mg/l Mn, 40 mg/l Al, 19 mg/l Ni, 9 mg/l Cr, 9 mg/l Pb, 9 mg/l Zn, 4 mg/l Cu and 10.3% free H_2SO_4. The pickle liquor additions were 0, 10 and 20 mg/l as Fe for separate periods of approximately 30 days each.

The mixed liquor suspended solids (MLSS) in the control reactor were maintained at 2000 to 2500 mg/l by sludge wasting. In the pickle liquor reactor, it was observed that the mixed liquor total iron concentration was in the range of 180 $\pm$ 30 mg/l Fe which would imply 345 mg/l as $Fe(OH)_3$ or 485 mg/l as $FePO_4$. Accordingly, the MLSS in the pickle liquor reactor was maintained at 2400-3000 mg/l.

The two activated sludge reactors were later operated on a synthetic sewage solution which allowed control of the influent phosphorus concentration as well as the pickle liquor additions, rather than dealing with random phosphorus influents as was the case with the raw sewage feed. The system could, therefore, come to equilibrium under different conditions of influent phosphorus and pickle liquor concentrations. Using this approach, the iron dosages to achieve different effluent phosphorus levels

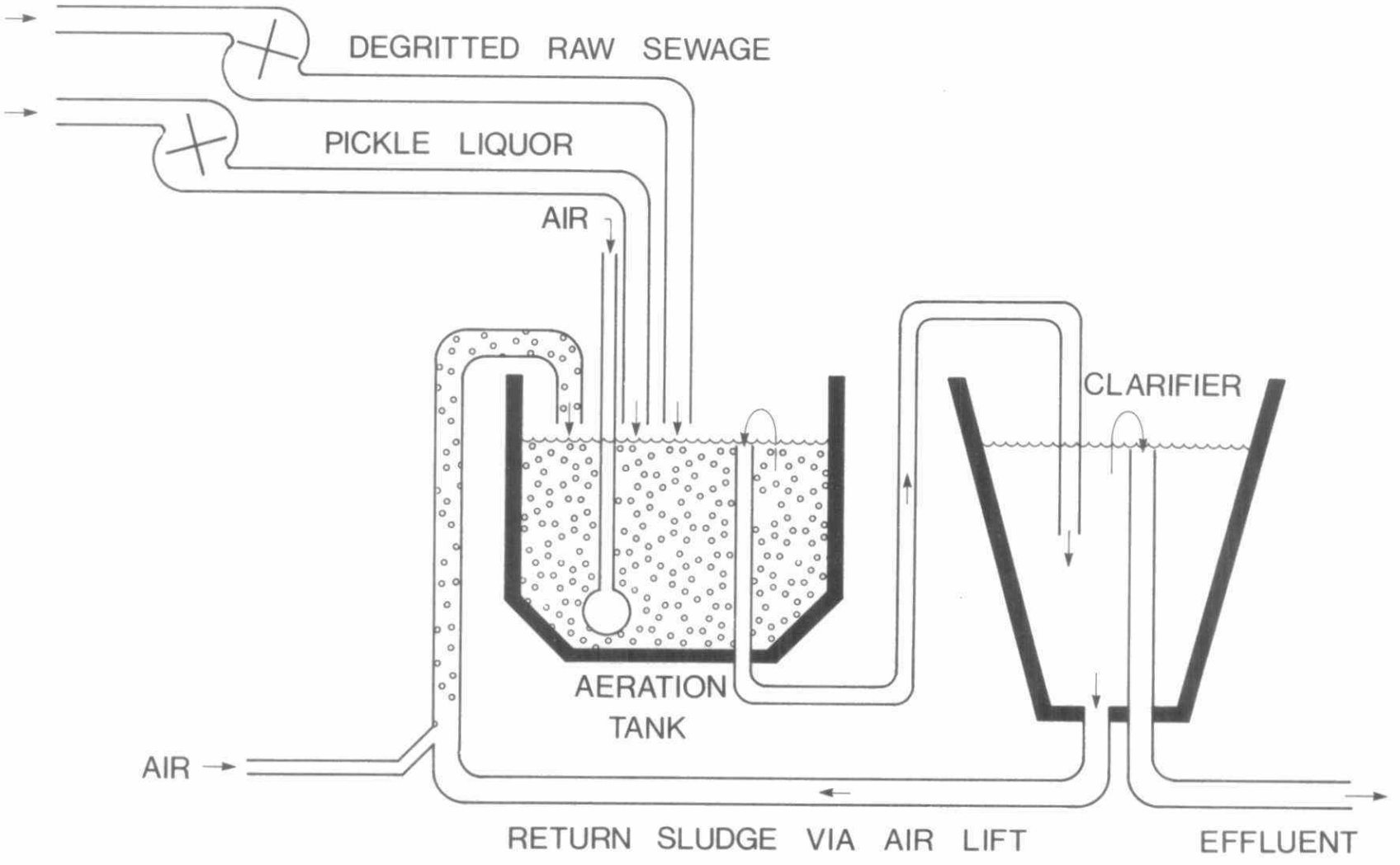


FIGURE 1 : SCHEMATIC OF LABORATORY ACTIVATED SLUDGE UNIT

could be determined, thus giving a better understanding of any iron: phosphorus stoichiometric relationships.

The flow rates were 30 ml/minute day and night (i.e. - retention times of 5 and 2 hours in the aeration tank and clarifier, respectively). The feed solution consisted of a mixture of 0.13 g/l Bacto Beef Extract, 0.22 g/l Bacto Peptone, 0.12 g/l NH_4Cl, 0.50 g/l dextrose, 0.31 g/l $NaHCO_3$, sufficient phosphate solution to give the desired phosphorus concentration, tap water and sulfuric acid adjusted to pH 7.5. The phosphate solution was mixed according to an approximate relationship suggested by Jenkins et al (1971) to give a ratio of PO_4^{3-} - P : $P_2O_7^{4-}$ - P : $P_3O_{10}^{5-}$ of 5:1:3 which is similar to that found in raw sewage. The bicarbonate and sulfuric acid were added to give the feed a buffering capacity similar to that of raw sewage (e.g. - Titration curves of the synthetic and raw sewage were almost identical.).

The pickle liquor additions were set at 6, 12 and 18 mg/l as Fe during the respective experimental periods. For each iron level, phosphorus concentrations in the feed were employed each for a period of one week. These phosphorus feed concentrations were set in the range of 3.5 to 12.8 mg/l. Due to a high concentration of filamentous bacteria or fungi in the mixed liquor, clarifier settling was generally very poor. The effluent samples were therefore filtered through a Whatman #1 filter paper immediately after sampling. Two days were allowed between changes in experimental conditions to allow equilibrium to be re-established.

2.4 PROCEDURES FOR PILOT PLANT EVALUATIONS OF THE FERRIC SULPHATE PRODUCT

A ferric sulphate solution (9-10% Fe) which had been prepared from a sludge incinerator ash raw material by The Electric Reduction Company of Canada Ltd. was tested in a phosphorus removal application utilizing the 20 Igpm chemical treatment pilot plant at the Wastewater Technology Centre. The pilot plant consists of flash mix (5 min), flocculation (20 min) and clarification (90 min) stages. The pilot plant was operated on degritted raw sewage from the Burlington Skyway Wastewater Treatment Plant, feeding liquid $Fe_2(SO_4)_3$ to the flash mix unit at a dosage of 25 mg/l as Fe for one week and 15 mg/l as Fe for a second week. The influent and effluent streams of the pilot plant were automatically sampled at hourly intervals, 24 hours per day. From the hourly samples, three 8-hour composite samples were prepared for the periods 00:00 to 8:00, 8:00 - 16:00 and 16:00 to 24:00 hours. The analyses performed on the influent and effluent wastewater samples are summarized in Table 1. The analytical procedures are described in Appendix C.

A total of ten separate jar tests were run during the course of the pilot plant experiments using Skyway raw sewage and dosages of $Fe_2(SO_4)_3$ of 0 to 30 mg/l as Fe. The flash mix, flocculation and settling times were matched to the corresponding pilot plant retention times. The total phosphorus removals were evaluated and subsequently compared to the pilot plant performance.

TABLE 1

ANALYSES PERFORMED ON PILOT PLANT INFLUENT AND EFFLUENT FOR THE $Fe_2(SO_4)_3$ STUDY

Biochemical Oxygen Demand (BOD_5)	Total Phosphorus
Total Organic Carbon (TOC)	Total Filtered Phosphorus
Suspended Solids (SS)	Chromium
	Copper
	Iron
	Manganese
	Zinc

As a matter of routine, total alkalinity, pH and hardness analyses were performed on 24-hour composites of the influent and effluent.

The sludge collected in the clarifier was sampled three times per day and a composite prepared from these samples. Total solids, total phosphorus, chromium, copper, iron, manganese and zinc determinations were made on the sludge samples.

2.5 PROCEDURES TO DETERMINE THE FATE OF HEAVY METALS DURING A FULL-SCALE PICKLE LIQUOR ADDITION

This phase of work was undertaken in conjunction with a phosphorus removal treatability study being conducted at the Dunnville

Wastewater Treatment Plant by R. V. Anderson Associates and Pollutech Pollution Advisory Services Ltd.. The phosphorus removal efficiency of the 1.7 MIGD activated sludge plant was evaluated for pickle liquor (from a local Dunnville industry) additions to the aeration tank.

A schematic diagram of the Dunnville plant is presented in Figure 2. Degritted raw sewage flows directly to an aeration tank with an average residence time of 4.5 hours, then to two parallel clarifiers with a mean residence time of 2.7 hours. After chlorination, the effluent discharges to the Grand River. Sludge from the secondary clarifiers is returned to the head of the aeration tanks with a small portion being wasted to the aerobic digester (≃ 12 days retention time). Digested sludge is periodically pumped to a thickener for further dewatering, with the thickened sludge being subsequently discharged to a lagoon. The digester and lagoon supernatants are returned to the head of the aeration tank. Pickle liquor additions during the treatability study were made at a point approximately 28 feet from the effluent end of the aeration tank.

To determine the background levels of heavy metals in the Dunnville raw sewage and the various plant streams and, subsequently, the fate of the heavy metals added with the pickle liquor, the following sampling program was devised:

(i) the influent and effluent (locations A and B in Figure 2) of the plant were sampled hourly, four-hour composites were prepared for the time periods 0:00 - 4:00, 4:00 - 8:00, 8:00 - 12:00, 12:00 - 16:00, 16:00 - 20:00 and 20:00 - 24:00;

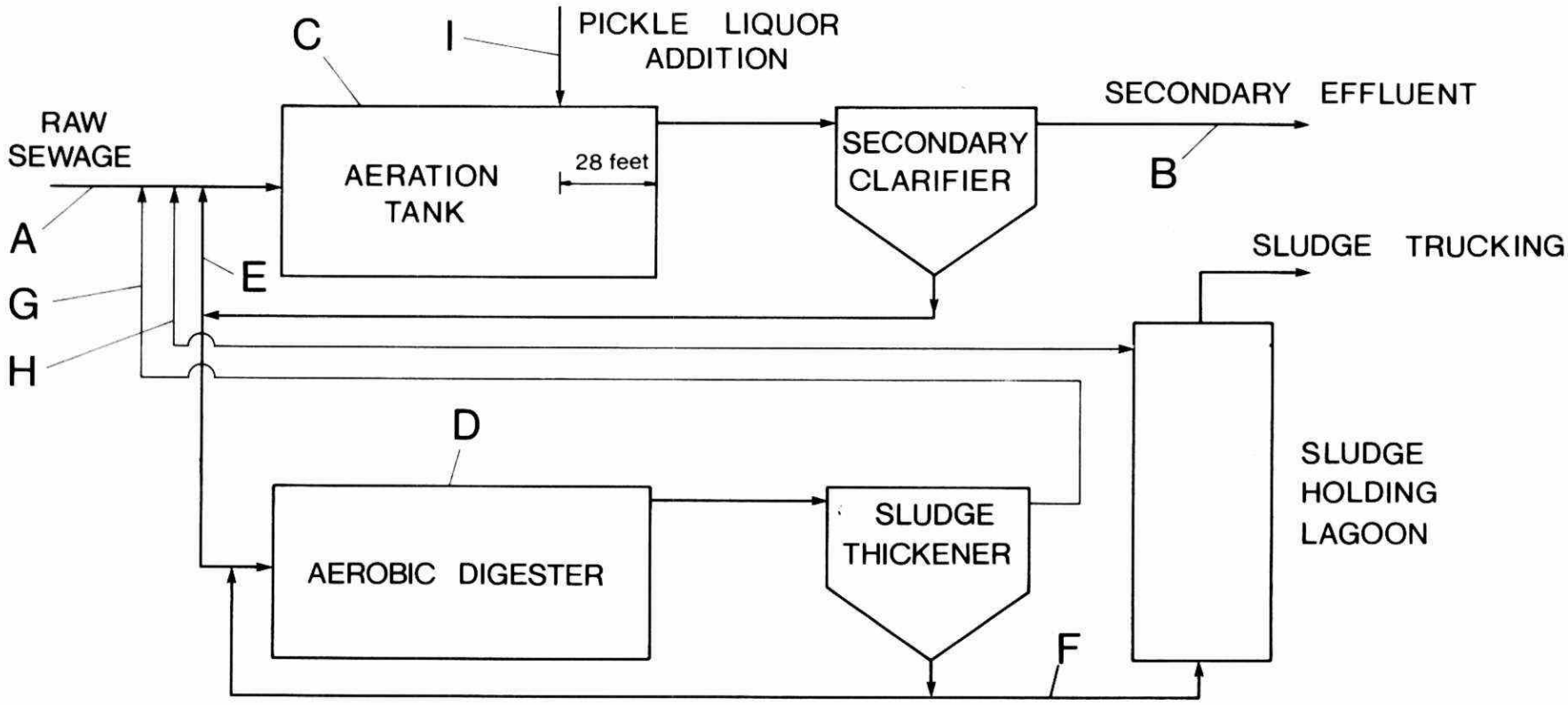


FIGURE 2 : SCHEMATIC FLOW DIAGRAM OF DUNNVILLE WATER POLLUTION CONTROL PLANT

(ii) two daily grab samples were composited for the aeration tank mixed liquor, aerobic digester sludge, return sludge, waste sludge, digester supernatant, lagoon supernatant and pickle liquor (if applicable). These locations are indicated, respectively, as C, D, E, F, G and H and I in Figure 2.

The sampling program was followed for six days prior to any pickle liquor additions, to assess baseline conditions, and for six days during pickle liquor additions. The plant was allowed to acclimatize to the pickle liquor addition for 2 - 3 weeks before the latter sampling period.

The samples collected during the baseline and pickle liquor addition periods were analyzed for the metals listed in Table 2. In addition, the suspended solids concentrations of all samples were determined. Since NTA may contribute to heavy metal transport through a wastewater treatment plant, periodic measurements were made of the NTA concentrations in the plant influent and effluent. NTA analytical procedures have been described by Traversy (1971).

TABLE 2

METAL ANALYSES PERFORMED ON DUNNVILLE SAMPLES

Aluminum	Iron
Arsenic	Manganese
Calcium	Mercury
Cadmium	Nickel
Chromium	Lead
Copper	Zinc

CHAPTER 3

RESULTS AND DISCUSSION

3.1 INVENTORY

A total of 141 companies were contacted about their waste products and a summary of the response is shown in Table 3.

TABLE 3

RESPONSE OF INDUSTRY TO THE REQUEST FOR WASTE SAMPLES

	ONTARIO	QUEBEC
Companies contacted	100 (71%)	41 (29%)
Responding -- no appropriate wastes	30 (30%)	14 (35%)
Responding and supplying waste products	37 (37%)	11 (26%)
Total reply	67 (67%)	25 (61%)
No reply	33 (33%)	16 (39%)

Overall Reply (65%)

Sending Samples (34%)

It is interesting to note that Ontario companies demonstrated a higher response and provided about 1.4 times more waste products than

Quebec companies. Of the 48 companies supplying waste products, most had only one appropriate waste, six had two, three had three and two had five, bringing the total to 68 samples. The survey was not designed to be exhaustive but to indicate the major types of waste products available. The types of wastes provided by the individual companies are indicated in Appendix A.

3.2 ASSESSMENT OF VARIOUS TYPES OF WASTE PRODUCTS

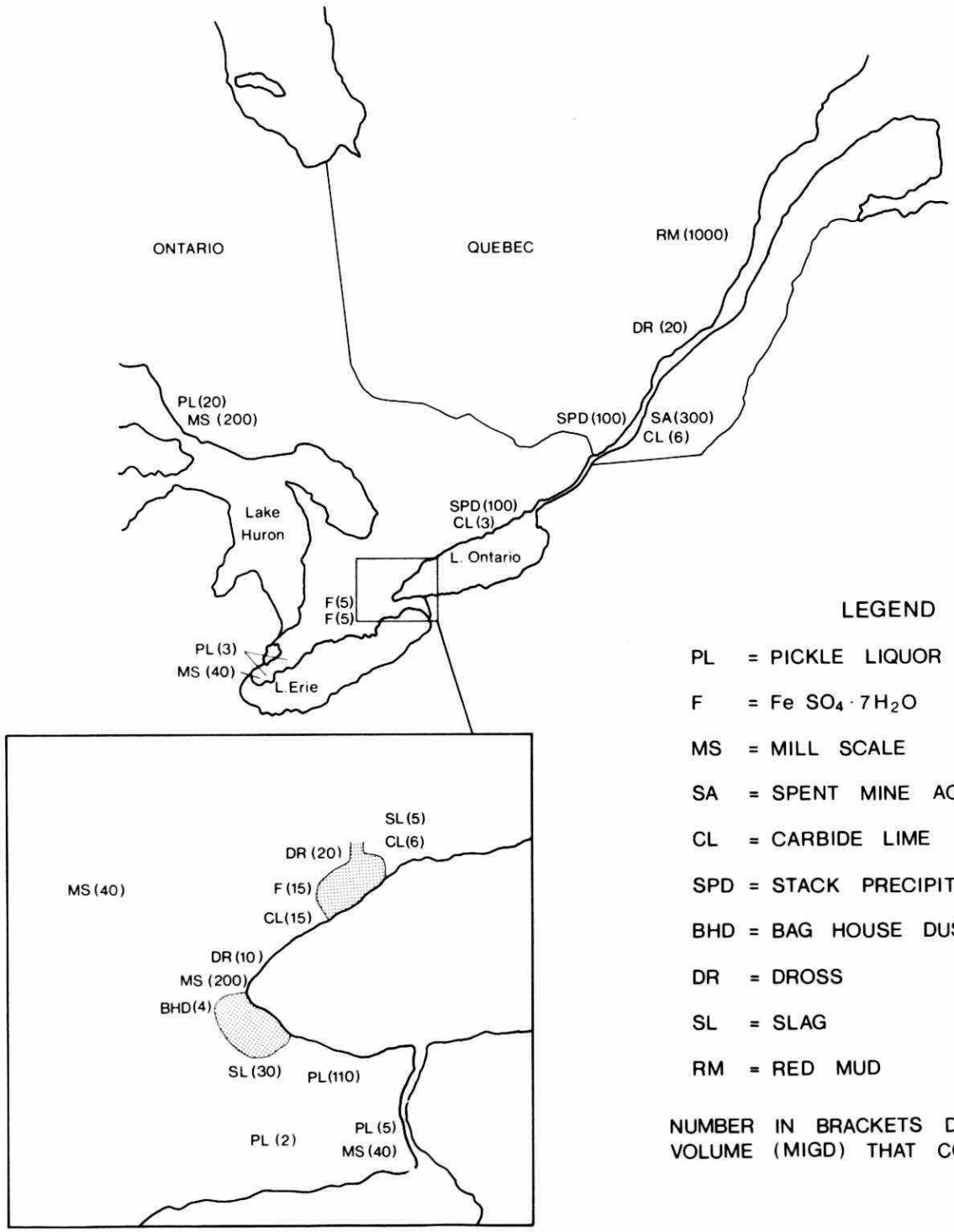
The assessment of the various waste products encountered in this study is summarized in Table 4 and the performance of the individual waste types are discussed in the subsequent Sections. The geographic locations of potentially useful waste products are indicated in Figure 3.

3.2.1 PICKLE LIQUORS

Pickle liquor is an acidic solution of 30 - 90 g/l ferrous iron, most frequently in an approximate 10% sulfuric acid solution. Other acids, (particularly hydrochloric), are occasionally encountered. It is probably the simplest waste to add to a wastewater on a large scale, requiring only a storage and feeding system and a supply of fairly reproducible iron-content pickle liquor.

For the pickle liquors evaluated on Skyway raw sewage, the phosphorus removals were optimum at a dosage of 20-30 mg/l as Fe, as this range consistently gave a supernatant phosphorus concentration of less than 1 mg/l. A typical jar test result for a pickle liquor is presented

FIGURE 3 : GEOGRAPHICAL LOCATION OF POTENTIALLY USEFUL INDUSTRIAL WASTE SOURCES



LEGEND

PL = PICKLE LIQUOR

F = $Fe\ SO_4 \cdot 7H_2O$

MS = MILL SCALE

SA = SPENT MINE ACID

CL = CARBIDE LIME

SPD = STACK PRECIPITATION DUST

BHD = BAG HOUSE DUST

DR = DROSS

SL = SLAG

RM = RED MUD

NUMBER IN BRACKETS DENOTES WASTEWATER VOLUME (MIGD) THAT COULD BE TREATED.

SUMMARY OF THE ASSESSMENT OF WASTE PRODUCTS

WASTE PRODUCT	COMPOSITION	DOSAGE REQUIRED FOR 1 mg/l EFFLUENT TOTAL PHOSPHORUS	OPTIMUM pH FOR PHOSPHORUS REMOVAL	GENERAL COMMENTS
Pickle Liquors 1) Atlas Steel Co. (2) 2) Algoma Steel Co. 3) North American Rockwell 4) Interlake Steel Products 5) Dominion Foundries and Steel 6) East Side Plating 7) Lundy Steel Products	30-90 gm/l Fe 4-40 mg/l Al 0.5-40 mg/l Cr 5-10 mg/l Cu 200-3500 mg/l Mn 20-25 mg/l Ni 4-10 mg/l Pb 9-13 mg/l Zn 5-15% H_2SO_4	20-30 mg/l as Fe	7 to 10	Can generally be used directly. Stainless steel pickling liquors are less suitable since they contain ≈ 20 gm/l Cr and 2 gm/l Ni.
Spent Acid Solutions 8) Canadian Titanium Pigments	20-25 gm/l Fe 3-6 gm/l Al 0.1-0.4 gm/l Cr 0.1-0.2 gm/l Mn a few mg/l Cu, Ni, Pb, Zn 20-25% H_2SO_4	20-30 mg/l as Fe	7 to 10	Must be neutralized before or during use. Additional iron could be dissolved by the free H_2SO_4.
$FeSO_4.7H_2O$ reclaimed from Pickle Liquors 9) Karemchemie Corp. 10) Firestone Steel Products 11) Dosco Ltd.	20-25% Fe 0.05% Mn 0.005% Cu 0.00% Zn 45% H_2O	20-30 mg/l as Fe	7 to 10	Insignificant pH reduction. Could possibly be handled in dry form.

TABLE 4 (Cont'd.)

WASTE PRODUCT	COMPOSITION	DOSAGE REQUIRED FOR 1 mg/l EFFLUENT TOTAL PHOSPHORUS	PHOSPHORUS REMOVAL	GENERAL COMMENTS
Carbide Lime (Acetylene Manufacture) 12) Domtar Ltd. 13) Toronto Iron Works 14) Union Carbide Ltd. 15) Canadian Oxygen Ltd. 16) Canadian Liquid Air 17) Liquid Carbonic Ltd.	52% Ca 0.5% Si 0.3% Fe 0.2% Al 0.1% Mg	0.5 gm/l slurry or ≈ 350 mg/l as available $Ca(OH)_2$	> 8.5	A gray slurry waste from acetylene production. Rather abrasive and difficult to pump.
Stack Precipitator Dust (Cement Production) 18) Canada Cement LaFarge Ltd. 19) Lake Ontario Cement Ltd.	25-30% Ca 1% Fe 1-2% Al 1% Mg 4-14% K	2 gm/l dust or ≈ 1100 mg/l as $Ca(OH)_2$	> 8.5	A white powder reclaimed by electrostatic precipitators.
Bag House Dusts (Steel Production) 20) Burlington Steel Co. 21) Dominion Foundries & Steel (2) 22) Steel Co. of Canada Ltd. (3)	Variable composition dependent on original production process.	0.2-0.6 gm/l of dust	> 8.5 for lime dusts	Fine airborne particles trapped in filter bags. Lime and iron based dusts exist but only the lime dusts are directly useful. Iron in these dusts is usually Fe_2O_3. Iron dusts were leached with H_2SO_4 to give a solution of 45 gm/l Fe and 42 gm/l Zn.

TABLE 4 (Cont'd.)

WASTE PRODUCT	COMPOSITION	DOSAGE REQUIRED FOR 1 mg/l EFFLUENT TOTAL PHOSPHORUS	PHOSPHORUS REMOVAL	GENERAL COMMENTS
Red Mud (Bauxite Leaching) 23) Aluminum Company of Canada Ltd.	8% Al 3.5% Ca 10% Fe 8% Si	5 gm/l red mud slurry	< 7 or > 9	A brick red sludge. The large volume required for P-removal will also produce a large increase in sludge volume. Effluent turbidity problems due to poor settling. Iron additions assist P-removal and settling.
Mill Scale (from steel making and forming) 24) Burlington Steel Co. 25) Galt British Forge Ltd. 26) Canada Forgings Ltd. 27) Dominion Forge Co. 28) Welmet Industries 29) Algoma Steel Co.	99% Fe_3O_4 0.5% Mn 0.2% C 0.03% S 0.01% P	not directly useful		Easily acid soluble (H_2SO_4 or HCl) to form a solution similar to a pickle liquor.
Dross (Aluminum Smelting) 30) Burlington Die Casting Ltd. 31) Reynolds Aluminum Co. 32) Reynolds Extrusion Co.	40% Al 30% Al_2O_3 30% NaCl	not directly useful		Can be leached in acid or alkali to form alum or sodium aluminate.

in Figure 4(a). Additional experimental results for several different pickle liquors are included in Figures B-1 through B-8 of Appendix B. For comparison, a typical jar test using the traditional iron precipitant $FeCl_3$ is presented in Figure 4(d).

Oxidation to Fe^{3+} was usually complete within about 20 minutes as evidenced by the precipitate changing colour from green to brown. This is in agreement with studies carried out at Harvard University (1970) that found that the half life of Fe^{2+} at 25°C was 4 minutes in solution under a partial pressure of 0.2 atmospheres of oxygen.

Examination of the removal vs. pH relationships in Appendix B showsthat the final pH (after pickle liquor addition) should be greater than 7 for consistently good phosphorus removals. Pickle liquors are therefore applicable to alkaline wastewaters since they generally lower the solution pH 0.1 to 0.5 units. However, the Rand Development Corp. (1971) found it necessary to add lime in conjunction with the pickle liquor, even with an alkaline wastewater of average pH of 7.6.

Of the six companies supplying pickle liquors, their combined output is estimated at 58,000 gallons per day at an average iron concentration of 60 g/l. At a wastewater dosage of 20 mg/l as Fe, these pickle liquors could conceivably treat 174 MIGD of sewage.

3.2.2 SOLID FERROUS SULPHATE

Dempter and Gomaa (1972) describe a process whereby ferrous

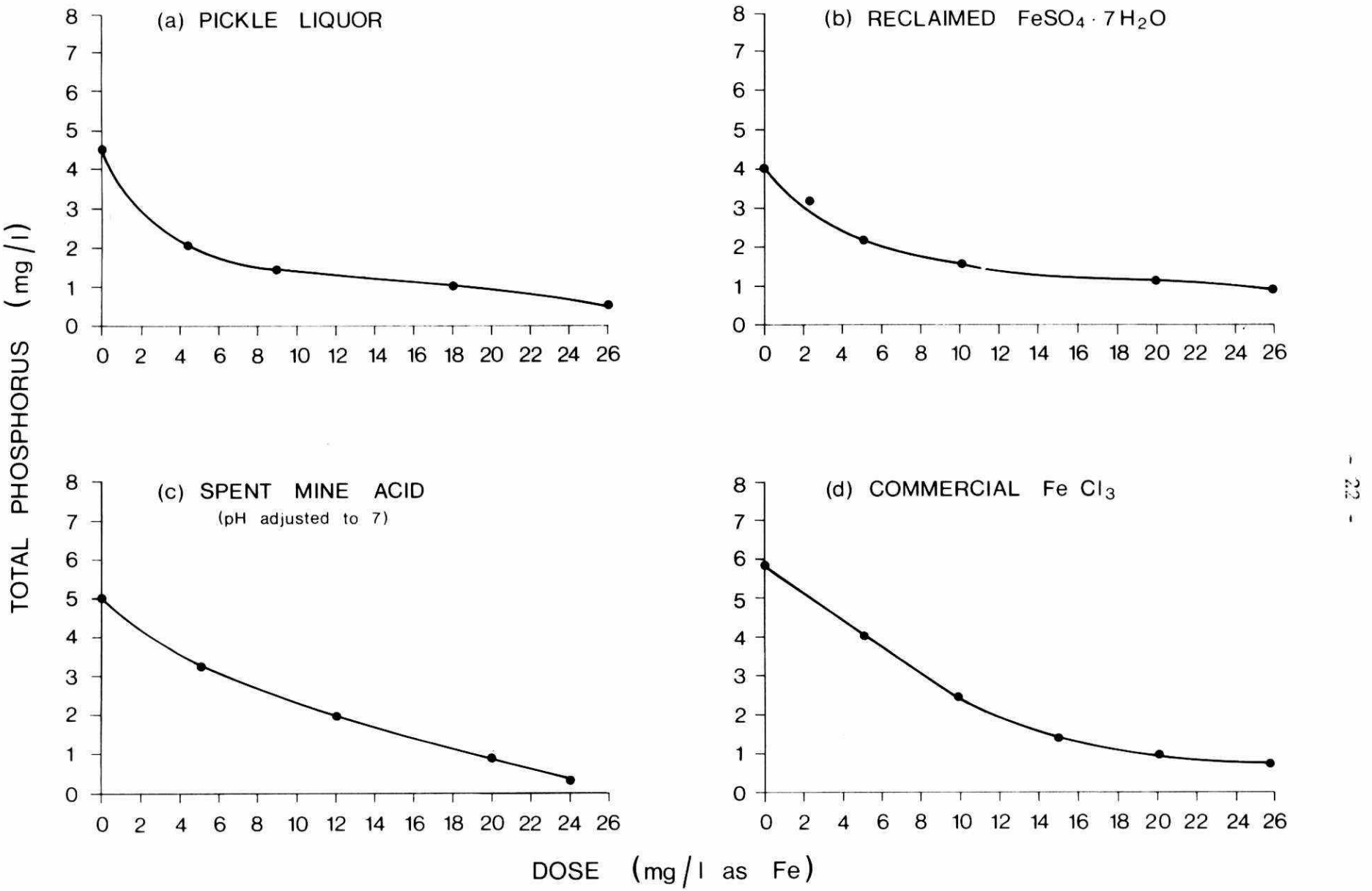

(a) PICKLE LIQUOR
(b) RECLAIMED $FeSO_4 \cdot 7H_2O$
(c) SPENT MINE ACID
(pH adjusted to 7)
(d) COMMERCIAL $FeCl_3$
TOTAL PHOSPHORUS (mg/l)
DOSE (mg/l as Fe)
0 1 2 3 4 5 6 7 8
0 2 4 6 8 10 12 14 16 18 20 22 24 26

FIGURE 4 : TYPICAL JAR TEST RESULTS FOR SOME IRON CONTAINING MATERIALS

sulfate can be recrystallized from sulfuric acid pickle liquors by cooling under reduced pressure. The sulfuric acid is thereby recovered for recycle to the pickling lines. Although a recovery process exists for hydrochloric acid pickle liquors, the iron by-product is Fe_2O_3 which has no direct utility. The ferrous sulphate crystals contain a comparable proportion of heavy metals and demonstrate similar phosphorus removal capabilities (on a unit iron content basis) as the original pickle liquors. The crystals may be redissolved and fed as a liquid or perhaps metered into the wastewater by a dry feeding system. Contrary to pickle liquor systems, there is no free acid added to the wastewater; consequently, the ferrous sulphate product may be applicable to more acidic wastewaters. Additions of 50 and 100 mg/l reclaimed $FeSO_4.7H_2O$ (10 and 20 mg/l as Fe) caused insignificant pH changes (< .05 units) in the wastewater. Oxygenation of the Fe^{2+} proceeded in a similar time frame to the pickle liquor. A typical jar test result is presented in Figure 4(b). Additional results are summarized in Figure B-9 of Appendix B.

At present, the sulfuric acid recovery process is used at a limited number of steel plants and approximately ten tons per day of ferrous sulphate are produced at 20-25% Fe which, at a dosage of 20 mg/l Fe, could treat 25 MIGD of sewage. However, a suitable market for this salt would probably stimulate further recovery activities and improve the overall economics of sulfuric acid recycle.

3.2.3 SPENT MINE ACIDS

Spent acidic leach solutions from mineral refining generally contain a smaller amount of iron (≃ 20 g/l) than pickle liquors and two to four times the free sulfuric acid. Direct addition for phosphorus removal is not practical since with a 20 mg/l iron addition to the wastewater, the effluent pH could fall as low as 3. This would definitely inhibit the activated sludge processes and, at the same time, poor settling of the iron-phosphate floc would occur. Additions of an alkali or possibly an alkaline waste to give a pH in the range of 7 in the wastewater will result in good phosphorus removals. See Figure 4(c) for a typical result at an adjusted pH of 7. Additional jar test results for the spent acid are presented in Figure B-11 of Appendix B. The neutralization aspect will be discussed further in Section 3.2.10.

Spent mine acids could be used as an acid source in which to dissolve additional iron. Certain spent acids, particularly from Northern Ontario mining operations, may contain radioactive substances such as radium and are likely unsuitable for phosphorus removal. The only potentially useful source of spent acid encountered in this study was in Quebec. This operation produces about 300,000 Igpd of waste leach solution at 20-23% Fe^{2+}. At a wastewater dosage of 20 mg/l Fe, this source alone would treat some 300 MIGD of sewage, if the pH reduction problems could be surmounted by dissolving more iron in the free acid or by neutralizing the free acid.

3.2.4 CARBIDE LIME

Carbide lime is a by-product from the manufacture of acetylene according to the following equation:

$$CaC_2 + H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

The calcium carbide used in this process is reasonably pure, resulting in lime that is relatively free of impurities. Since excess water is used in acetylene production, the lime is in a slurry. Contaminants are generally small amounts of silica, carbon, magnesium, iron and aluminum. (See Table 4.) A faint odour of acetylene is also apparent in fresh samples.

Carbide lime gave some of the most consistent and reproducible phosphorus removals of all the materials tested. Dosages of 400 - 500 mg/l carbide lime were required to raise the pH of the wastewater to about 10 and resulted in a residual phosphorus of less than 1 mg/l. See Figure 5(a) for a typical jar test and Table 4 for further data on carbide lime. Results of additional jar tests are presented in Figure B-10 of Appendix B.

The lime slurry is particularly abrasive and problems may be encountered with feed pumps. The companies surveyed tended to use centrifugal or air lift pumps to handle this material.

The quantities of carbide lime produced by the respondents to this survey are in the order of 75 tons per day. At a dosage of 500 mg/l of the slurry, this quantity could conceivably treat 30 MIGD of wastewater,

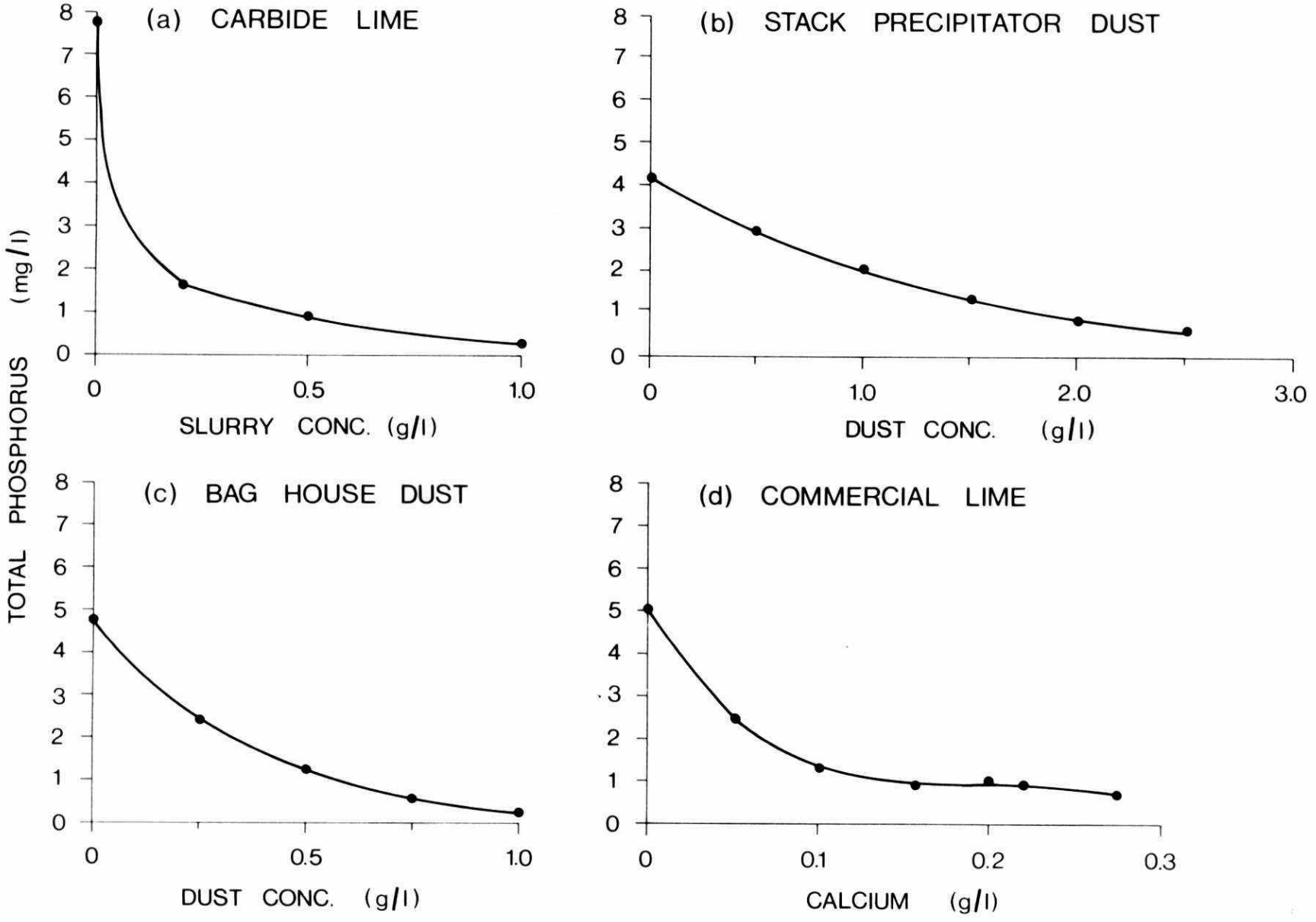


FIGURE 5 : TYPICAL JAR TEST RESULTS FOR SOME LIME CONTAINING MATERIALS

if the handling problems could be surmounted.

3.2.5 STACK PRECIPITATOR DUSTS

The production of cement is a thermal process which can inject considerable particulate matter into the atmosphere. These particles are generally precipitated electrostatically or mechanically and are considered as waste. The resultant material is a white, dry powder containing about 30% Ca which will hydrolyze when introduced into a wastewater to give large settleable flocs and good phosphorus removal. However, large dosages of about 2 g/l of the dust (1100 mg/l as $Ca(OH)_2$) were necessary to give a pH of 9.5 and less than 1 mg/l residual phosphorus in the Skyway raw sewage. These dosages result in a large increase in sludge volume and would complicate any sludge disposal operations. A typical jar test is presented in Figure 5(b). Several additional jar test results are presented in Figure B-12 of Appendix B.

Impurities in this waste include small quantities of magnesium, aluminum and iron and a rather large quantity of potassium. See Table 4 for approximate analyses. The sources surveyed produce about 250 tons of the dust daily and, if used for phosphorus removal, would be able to treat about 25 MIGD of wastewater.

3.2.6 Bag House Dusts

Bag filtering is a common method of recovering particulates from air discharges and is usually associated with the steel industry.

These dusts may be either lime-based (30-45% Ca) or iron based (35-45% Fe). The lime-based dusts hydrolyze quickly when added to wastewater and behave similarly to the stack precipitator dusts. A dust dosage of about 600 mg/l was necessary for effective phosphorus removal. See Figure 5(c) for a typical jar test result. Other results are presented in Figure B-13 of Appendix B. Iron in these dusts is generally present as Fe_2O_3 and is inert to the phosphorus compounds encountered in sewage. It can be acid leached but considerable zinc will also dissolve. For example, one dissolution test at room temperature, using spent mine acid and an iron-laden bag house dust, gave a solution of 45 g/l of iron and 42 g/l of zinc after two days of leaching.

The industries surveyed produce about 15 tons/day of bag house dusts of which about two-thirds are the useful lime dusts. This quantity could serve to treat 4 MIGD of wastewater.

3.2.7 Red Mud

Red mud is the waste product from the caustic leaching of bauxite ores. It is a brick red sludge containing iron, aluminum, calcium and silica. The liquid portion of the sludge has a pH of about 12. In large dosages of 5 g/l, it will effect reasonably good phosphorus removal, but is quite variable in its action, depending on the nature of the wastewater. For example, in about 10% of the jar tests, red suspended matter remained in the supernatant causing a turbidity problem. The removal vs. pH relationships for red mud (Appendix B) indicate that

the addition of an acid or alkali will assist in phosphorus removal. It was noted that iron additions of 2 or more mg/l assist in the settling of the red suspended matter. Again, as with stack precipitator dusts, the large additions necessary for good phosphorus removal produced a large increase in sludge volume.

Verghese (1973) has experimented with a process whereby red mud is treated with sulfuric acid to pH 6 to 8 and the solid material is allowed to settle. The dried precipitate, when added to wastewater at a dosage of 100 - 200 mg/l effects good phosphorus removal. A more manageable quantity of sludge should result using this method.

Red mud is presently being generated at the rate of 1500 - 2000 tons per day. At a dosage of 5 g/l to the wastewater, and assuming sludge problems could be circumvented, it could treat close to one billion gallons per day. Because of the large quantities required and the remote location of the red mud, transportation costs would be unduly high.

3.2.8 Mill Scales

Mill scale is the oxide material that flakes off iron and steel when it is hammered or rolled and is the substance that dissolves during pickling operations. It varies in size from particles 1/4" in diameter to a fine dust, is predominantly Fe_3O_4 and does not appear to be directly useful for phosphorus removal. However, it is easily acid soluble to produce a solution similar to a pickling liquor which could be conveniently used for phosphorus removal.

The companies surveyed produced some 50 tons per day of mill scale at an average of 80% iron. Assuming that the iron in the mill scale can be dissolved and fed as a pickle liquor at the usual dose of 20 mg/l as Fe, it would treat about one billion gallons per day of sewage. Scott (1973) discusses in detail the economic aspects of producing iron salts from mill scales and other low-cost iron-containing waste materials.

3.2.9 Other Waste Products

Dross is a waste from the smelting of aluminum and is formed by the addition of sal-ammoniac to the melt which causes impurities to float to the surface. It is about 40% Al, 30% Al_2O_3 and 30% NaCl. The aluminum and alumina are either acid or alkali soluble, resulting, respectively, in alum or aluminate; however, a better yield of aluminum and separation of metals can be obtained using an alkaline leach. Twelve-hour slurrying of 1.0 gm dross in 0.01 N HCl and 0.01 N NaOH gave, respectively, 2 and 5 g/l of Al in the supernatants. Although the dross itself is not useful, both these supernatants were capable of effecting good phosphorus removals. This survey found about a 10 ton/day production of dross which, after an alkaline leach, could treat some 50 MIGD of wastewater.

Other lime wastes are generally slags which have varying degrees of utility for phosphorus removal. The most useful slag tested contained 36% Ca, 6% Si, 5% Mg, 4% Mn, 0.4% Al and 0.2% Fe. It hydrolyzed rapidly in the wastewater to give a good floc. However, 1.0 to 1.5 g/l slag was

necessary to achieve a pH of 9 and a 1 mg/l phosphorus residual in the effluent. Undoubtedly, this would cause a significant sludge-handling problem. The slag referred to above is produced at the rate of 140 tons per day and, at a dosage of 2 g/l, it could treat approximately 35 MIGD of sewage.

3.2.10 Combinations of Waste Products

Some waste product combinations were tested in this survey and some of the combinations demonstrated a potential utility for phosphorus removal.

Spent mine acids used in conjunction with carbide lime gave good phosphate removals at a pH of 6 or greater, as shown in Figure 6. The effect of the lime is to neutralize the acid and it likely removes little phosphorus itself below pH 8. An iron dosage of 20 mg/l, using spent mine acid would require about 200 mg/l carbide lime to give a pH of 6 and about 250 mg/l to give a pH of 7. However, residual phosphorus concentrations as low as 0.1 mg/l were obtained by this method at a reasonable effluent pH.

Red mud is assisted in its action by acid or alkali or iron additions. When both red mud and spent mine acid were added to the wastewater, the result was a better settling floc and good phosphorus removal at effluent pH values suitable for discharge. Figure 7 relates residual phosphorus and pH to the additions of red mud and spent acid. The particular set of jar test conditions [i.e., 2 grams of red mud and 0.3 ml

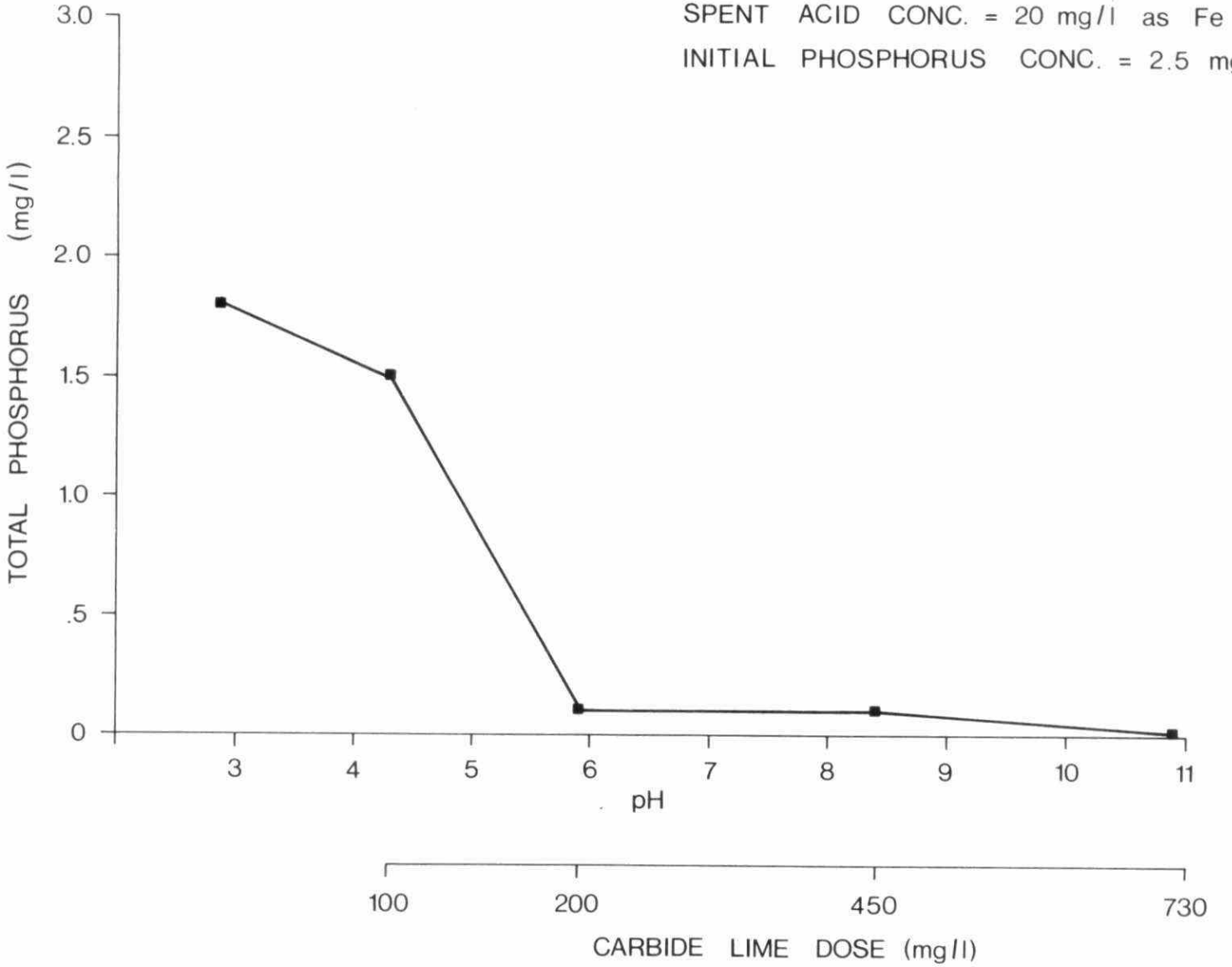


FIGURE 6 : EFFECT OF CARBIDE LIME NEUTRALIZATION (pH INCREASE) ON PHOSPHORUS REMOVAL BY SPENT ACID

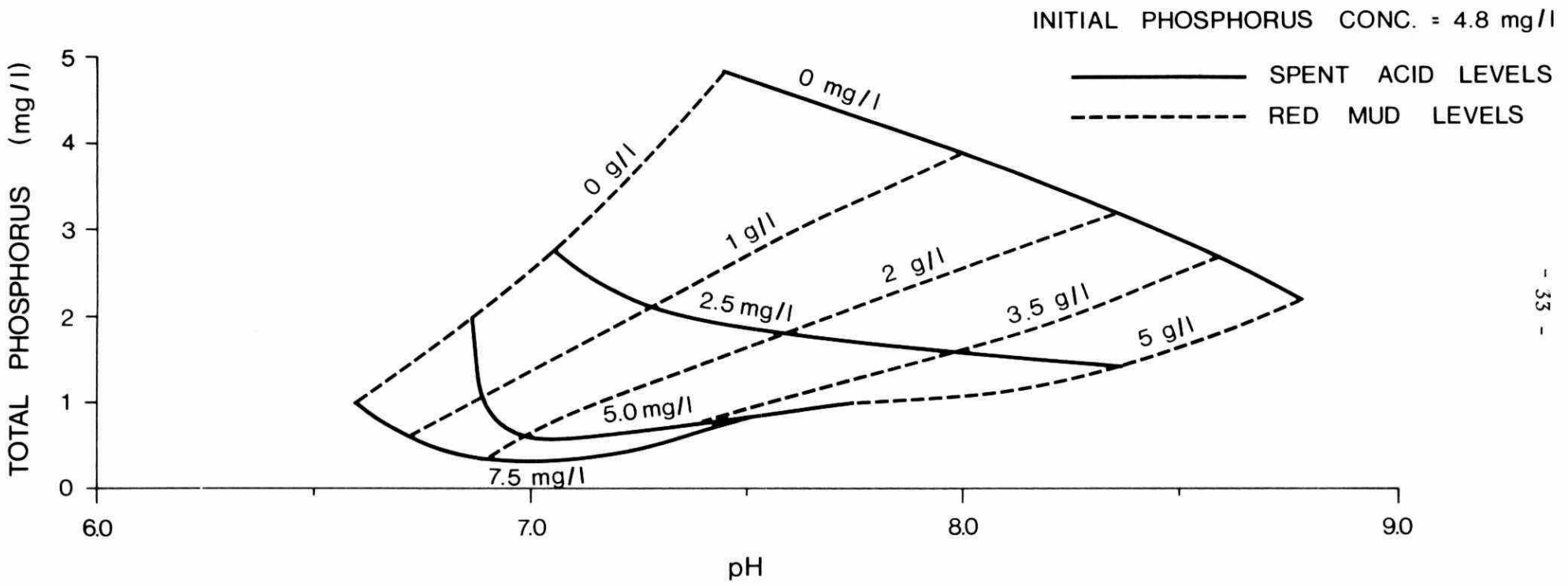


FIGURE 7 : EFFECT OF RED MUD - SPENT ACID COMBINATIONS ON RESIDUAL PHOSPHORUS AND pH

(7.5 mg Fe) spent acid per litre of wastewater] gave an effluent of pH 7 and .3 mg/l residual phosphorus. The use of red mud, either directly or in combination with other wastes, still entails a large increase in sludge volume.

3.3 EFFECTS OF PICKLE LIQUOR ADDITIONS ON A LABORATORY-SCALE ACTIVATED SLUDGE PROCESS

3.3.1 Iron Accumulation

The iron concentrations in the two continuous laboratory-scale activated sludge plants were determined at various points in the units, and the (daily samples for 30 days) results are summarized in Table 5. These results are from the period of pickle liquor addition at 10 mg/l as Fe. Most of the iron present in the various streams is in the ferric state, indicating that the oxidation of pickle liquor Fe proceeded to completion in the aeration tank. This is not unexpected and is in agreement with the work carried out at Harvard University (1970), and others, which report rapid oxidation of Fe^{2+} in the presence of oxygen.

Essentially all of the added iron accumulated in the mixed liquor solids and, consequently, total iron concentrations of the control and pickle liquor effluents were almost identical.

3.3.2 Phosphorus Removal

The phosphorus removal performance of the activated sludge units is summarized graphically in Figure 8 for the periods of 0, 10 and

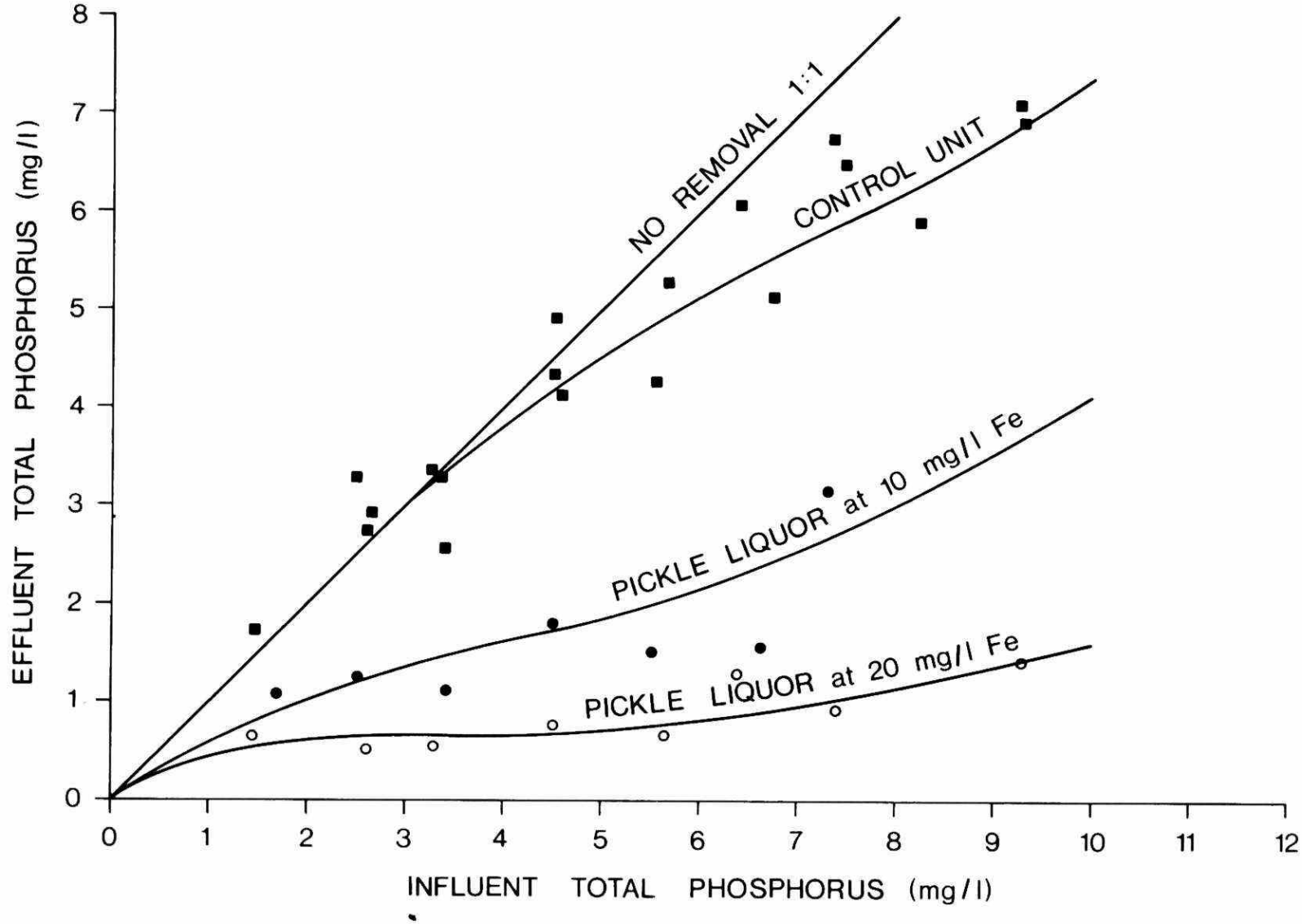


FIGURE 8 : PHOSPHORUS REMOVAL BY CONTROL AND PICKLE LIQUOR ACTIVATED SLUDGE UNITS TREATING RAW SEWAGE

TABLE 5

Iron Concentrations in Continuous Flow Activated Sludge Units

Location	Control Reactor		Pickle Liquor Reactor	
	Fe^{2+} [1]	Total Fe	Fe^{2+}	Total Fe
Mixed Liquor	0.2	51	8.0	180
Mixed Liquor Supernatant	N.D.	0.2	N.D.	0.1
Return Sludge	N.D.	130	N.D.	380
Raw Sewage	N.D.	0.47	N.D.	0.47
Effluent	N.D.	0.47	N.D.	0.41

N.D. -- non detectable

[1] -- All values in mg/l

20 mg/l as Fe pickle liquor additions to the wastewater. The influent to these activated sludge plants was raw sewage which varied in phosphorus content over a range of 1 to 10 mg/l. The data were grouped by averaging the results for influent phosphorus in the ranges 1-2, 2-3 mg/l, etc., and, similarly, averaging the influent concentrations corresponding to these influents.

It is apparent from Figure 8 that some phosphorus removal occurs without pickle liquor additions. This removal is generally about 5 to 25% of the influent and is apparently due to the small metal ion concentration in the sewage causing precipitation, plus the phosphorus requirements of the activated sludge organisms. The addition of pickle liquor to the system, as expected, caused a marked decrease in effluent phosphorus concentrations.

The results indicate that a pickle liquor dosage of 10 mg/l as Fe will not consistently reduce the effluent phosphorus concentration to less than 1 mg/l. However, at a dosage of 20 mg/l as Fe, the effluent phosphorus concentration was less than 1 mg/l except when influent concentrations exceeded 7-8 mg/l phosphorus.

Phosphorus removal data from the periods of synthetic feed (i.e., controlled phosphorus levels) are presented in Table 6 and are summarized graphically in Figure 9. As expected, greater iron dosages resulted in lower phosphorus concentrations in the effluent, while greater influent phosphorus levels resulted in a high phosphorus effluent. It should be noted that a greater removal efficiency was observed using synthetic sewage as feed and this was undoubtedly due to the fact that the poor settling caused by filamentous bacteria necessitated filtration of the samples through a Whatman #1 filter paper.

These data show that a 1 mg/l soluble phosphorus residual in the effluent could be achieved with each of the iron dosages tested provided that they are matched to the appropriate strength influent. For

TABLE 6

PHOSPHORUS REMOVAL DATA FOR SYNTHETIC FEED CONDITIONS

Fe Addition (mg/l)	Feed P (mg/l)	Control Effluent P (mg/l)	Pickle Liquor Effluent P (mg/l)
6	4.28	3.80	1.02
6	8.50	7.18	3.31
6	12.30	10.97	7.33
12	3.52	3.25	0.48
12	8.20	7.23	0.93
12	9.58	9.24	2.52
12	10.20	9.20	3.20
12	12.80	11.10	5.90
18	4.10	3.92	0.31
18	8.60	8.68	0.91
18	11.74	11.28	2.74
18	12.50	12.27	2.90

example, a dosage of 6 mg/l as Fe will give less than 1 mg/l soluble phosphorus in the effluent up to an influent concentration of 3.75 mg/l P, 12 mg/l as Fe up to 6.5 mg/l P influent and 18 mg/l as Fe up to 9.25 mg/l P influent.

If the phosphorus available for pickle liquor precipitation is considered as that not removed naturally by activated sludge organisms and background metal ions in the sewage (i.e., phosphorus in the control

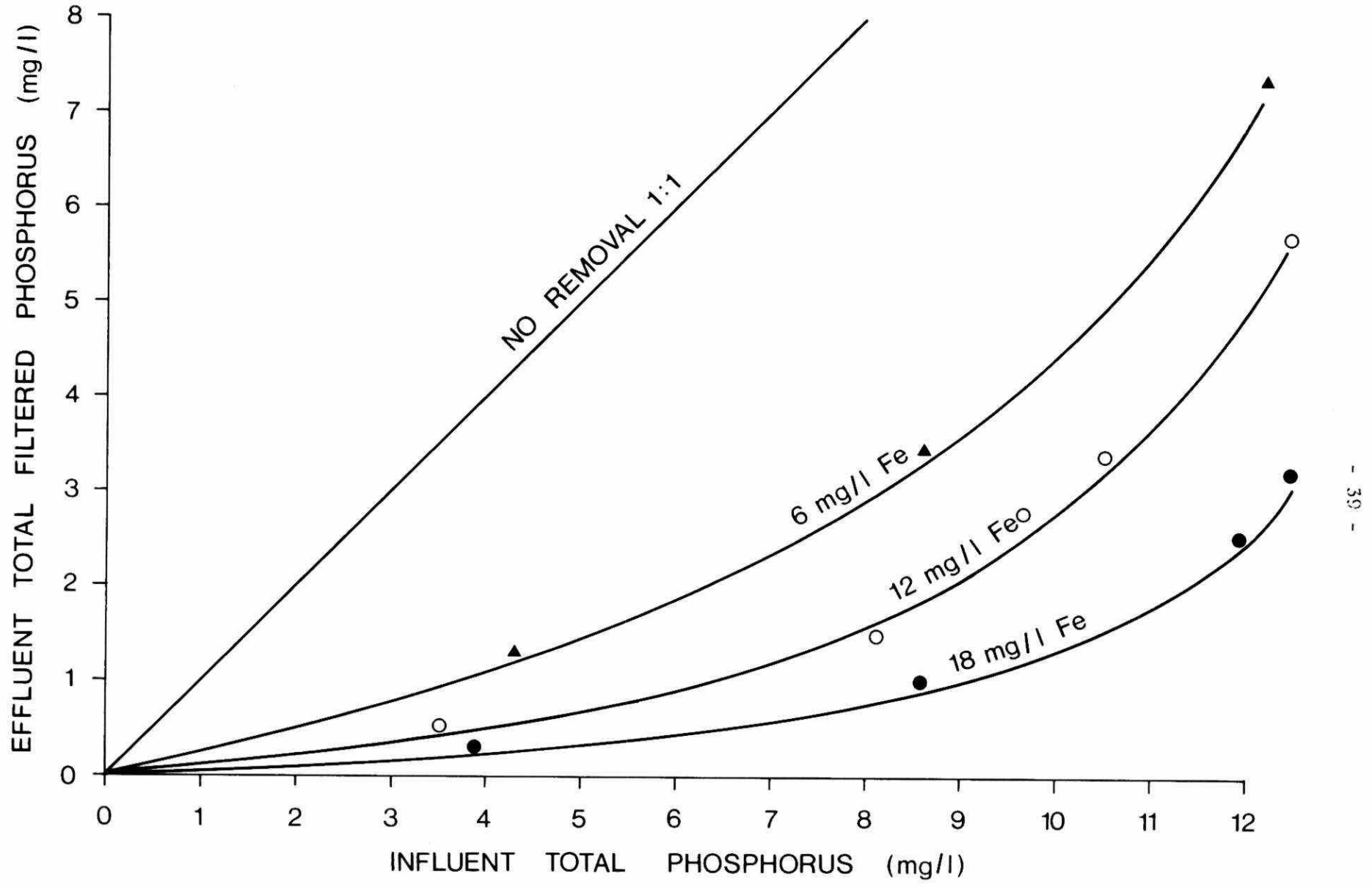


FIGURE 9 : PHOSPHORUS REMOVAL BY PICKLE LIQUOR ACTIVATED SLUDGE UNITS TREATING SYNTHETIC SEWAGE

unit effluent), phosphorus removal per unit of iron added may be computed. This ratio expressed on a molar basis is plotted vs. control effluent phosphorus in Figure 10. As the control effluent increases, the ratio tends to 1.0, indicating that the reaction stoichiometry is 1:1 provided that excess phosphorus is present. At higher iron dosages of 12 and 18 mg/l, some iron is probably ineffective due to precipitation as ferric hydroxide.

3.3.3 pH Reductions

The addition of pickle liquor caused the pH of the aeration tanks and effluent to be lowered slightly. The average pH of the raw sewage was 7.5 as was that of the control aeration tank and effluent. At a 10 mg/l iron addition, the pH of the aeration tank and effluent averaged 7.2 and, at a 20 mg/l iron addition, the aeration tank pH averaged 6.9 and the effluent pH 7.0.

3.3.4 COD and Nitrogen Removal

Chemical oxygen demand (COD) and various nitrogen species were determined on the influent and effluent of the control and pickle liquor reactors to determine whether there was any upset in the carbon and nitrogen removals due to the pickle liquor additions.

Sewage from the Burlington Skyway Treatment Plant fed to the laboratory reactors had an average COD over the duration of this study of 116.4 mg/l. The average effluent COD's from the control and pickle

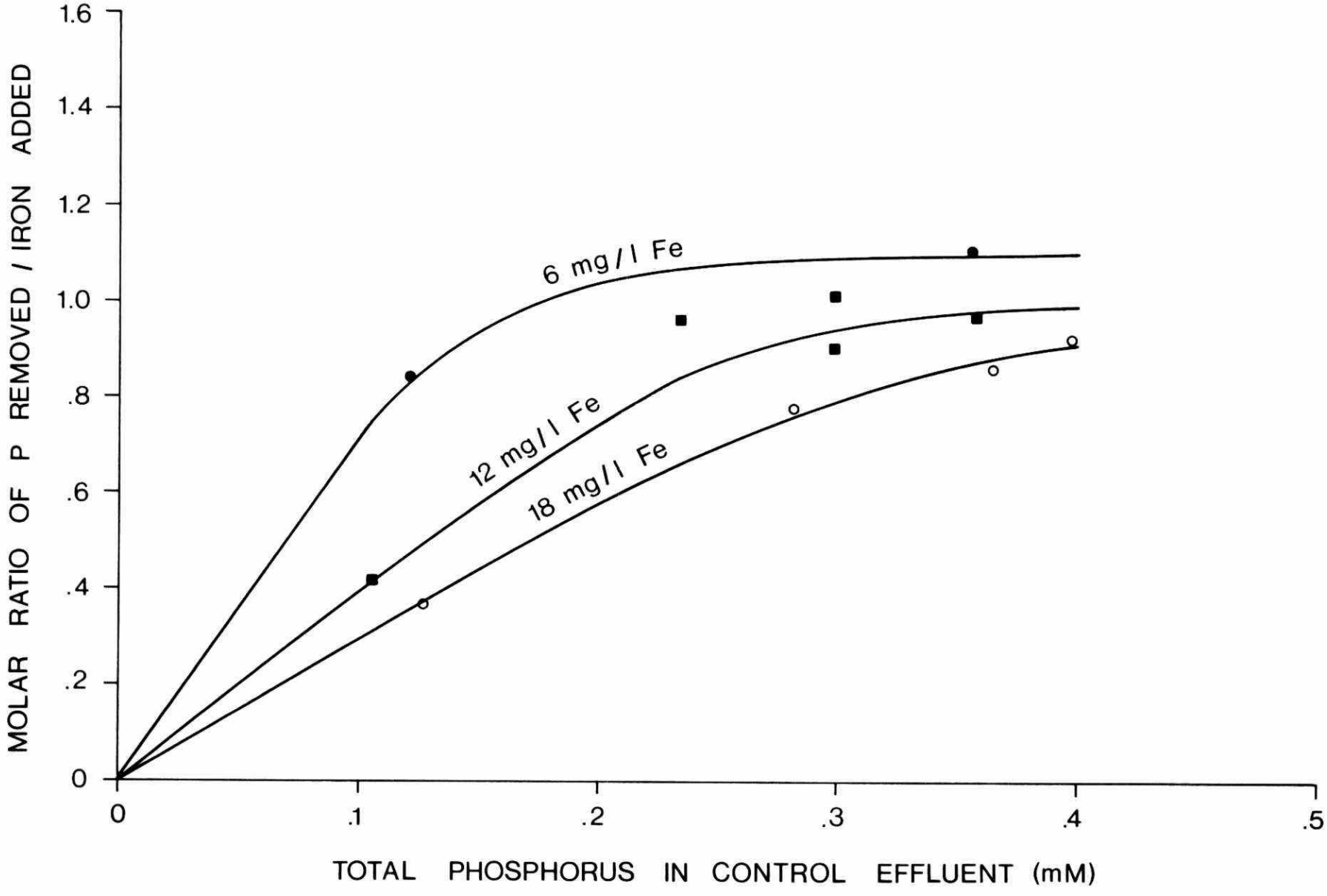


FIGURE 10 : MOLAR RATIO P / Fe vs PHOSPHORUS AVAILABLE FOR REMOVAL

reactors were 35.6 and 33.9 mg/l, respectively, to give per cent removal of 69.5 and 70.9%. These data are presented in Table 7 and are averages for all periods of pickle liquor addition when raw sewage was used as the feed. There was no noticeable difference in COD removal between the periods of 10 and 20 mg/l iron additions.

TABLE 7

COD REMOVAL BY ACTIVATED SLUDGE UNITS

COD RANGE	AVERAGE INFLUENT	AVERAGE CONTROL EFFLUENT	AVERAGE P. L. REACTOR EFFLUENT
0-50	34.4	32.3	27.4
50-100	72.5	32.4	31.1
100-150	129	37.8	34.1
150-200	179	39.5	38.5
200-300	221	39.6	31.0
300-400	344	38.5	32.7

All values in mg/l

Total Kjeldahl Nitrogen (TKN) which includes ammonia and organic nitrogen and filtered (.45 μ) nitrate and nitrite, was determined on 19 successive samples of influent and both effluents. The raw sewage had an average TKN of 18.8 mg/l and 0.13 mg/l NO_3^--N. No influent or effluent

sample had greater than 0.1 mg/l NO_2^--N. The nitrogen data for the period of 10 mg/l iron addition are presented in Table 8.

TABLE 8

TOTAL NITROGEN REMOVAL BY ACTIVATED SLUDGE UNITS

	Raw Sewage	Control Effluent	Pickle Liquor Effluent
TKN (mg/l)	18.8	4.8	3.9
NO_3^- + NO_2^- (mg/l)	0.1	12.4	14.5
Total N (mg/l)	18.9	17.2	18.4
Nitrogen Removed (mg/l)		1.8	0.5
% Removal		9.8	2.8

The reactor receiving pickle liquor additions demonstrated a lower total nitrogen removal than the control reactor. It is difficult to determine the reason for this, since the study was of such short duration. More detailed studies would be necessary before definite conclusions can be drawn regarding the effect of pickle liquors on nitrogen removal by activated sludge organisms. It should be noted, however, that the pickle liquor did not affect the nitrification capability of the activated sludge, (i.e., about 70% of the TKN was converted to nitrate-nitrite in each reactor).

3.3.5 Effluent Heavy Metals

Samples from the control and pickle liquor reactors were periodically analyzed for heavy metals, including Cr, Cu, Fe, Mn, Ni, Pb and Zn.

TABLE 9

FATE OF HEAVY METALS IN CONTROL AND PICKLE LIQUOR REACTORS

	Cr[1]	Cu	Fe	Mn	Ni	Pb	Zn
Pickle Liquor	9.0 mg/l	3.5 mg/l	60.0 g/l	116 mg/l	18.6 mg/l	9.2 mg/l	8.6 mg/l
Raw Sewage	7.9	51.1	0.46 mg/l	91.0	3.8	27.0	158.6
Addition due to Pickle Liquor	1.5	0.58	10.0 mg/l	1.9	3.1	6.3	1.5
Total Metals Input	9.4	51.7	10.5 mg/l	92.9	6.9	33.3	160.1
% Addition due to P.L.	15.9	1.1	95.4	2.	44.5	18.9	0.9
Control Effluent	5.7	42.6	0.47 mg/l	25.4	5.0	17.3	129.7
P.L. Reactor Effluent	3.3	30.1	0.41 mg/l	13.8	4.7	14.4	71.4
% Removal in Control	27.8	16.6	0.9	72.1	-31.1	35.9	18.2
% Removal in P.L. Reactor w.r.t. Raw Sewage	58.2	41.1	11.7	84.8	-23.0	46.7	55.0
% Removal in P.L. Reactor w.r.t. Total Metals Input	64.9	53.6	96.1	84.9	31.8	56.8	55.4

([1] -- All values in µg/l unless otherwise noted)

These metals were present in varying quantities in the raw sewage and were also added with the pickle liquor. The samples were taken during the period of 10 mg/l iron addition. Concentrations of the seven metals in the influents and effluents, percent contributions from the pickle liquor, and percent removals are presented in Table 9.

Except for iron and nickel, the metals loadings to the sewage due to the pickle liquor were less than 20% of the total metals input from raw sewage. In the control reactor, net metal accumulation occurred except for the iron and nickel. In the case of nickel, this may be due in part to the transport of a soluble NTA-Ni complex (Bjorndal et al, 1972). In the pickle liquor reactor, the effluent metals concentrations were, in all cases, lower than the control and, except for nickel, lower than in the raw sewage. This net metal removal is quite probably due to the sorptive properties of the ferric hydroxide and activated sludge flocs and has been documented by Wilms et al (1972) and others. Overall, the pickle liquor additions increased heavy metals removal in spite of the fact that some metals were being added with the pickle liquor.

3.4 RESULTS OF PILOT PLANT EXPERIMENTS ON THE $Fe_2(SO_4)_3$ PRODUCT

Since the $Fe_2(SO_4)_3$ material was a potential phosphorus removal precipitant produced from a sludge incinerator ash raw material and contained significant levels of certain heavy metals, the pilot plant experiments were designed to (i) evaluate its wastewater treatment capabilities and (ii) determine the fate of the heavy metals during the treatment process.

3.4.1 Removal Characteristics

The average total phosphorus, suspended solids and BOD concentrations in the pilot plant influent and effluent during the 25 and 15 mg/l as Fe ferric sulphate additions are summarized in Table 10. Standard deviations (N = 15) of each mean are indicated in parentheses. Percent removals are also listed for each characteristic.

The $Fe_2(SO_4)_3$ proved to be an efficient precipitant for phosphorus and the pilot plant results showed that a dose slightly in excess of 15 mg/l as Fe was required to achieve an effluent total phosphorus level of 1 mg/l. The jar test results were in good agreement with the pilot plant experiments -- i.e., the average (over 10 jar tests) $Fe_2(SO_4)_3$ dose required to achieve a 1 mg/l residual total phosphorus level was 15.5 mg/l as Fe. The average initial total phosphorus concentration for the jar tests was 4.1 mg/l. Due to the coagulative characteristics of the $Fe_2(SO_4)_3$, good removals of suspended solids and BOD were also observed.

The results obtained in the pilot plant runs were not unexpected and the use of $Fe_2(SO_4)_3$ for phosphorus removal and wastewater treatment has been documented by several investigators over the past 4 decades -- for example, see early summary compiled by Pearse et al (1935).

3.4.2 Fate of Heavy Metals

The $Fe_2(SO_4)_3$ product contained relatively high levels of certain heavy metals which had also been extracted from the sludge incinerator ash along with the iron. The analysis of the batch of $Fe_2(SO_4)_3$ used in

the pilot experiments is presented in Table 11.

TABLE 10

REMOVAL CHARACTERISTICS OF $Fe_2(SO_4)_3$ PILOT PLANT

Characteristic		$Fe_2(SO_4)_3$ at 25 mg/l as Fe	$Fe_2(SO_4)_3$ at 15 mg/l as Fe
BOD	Influent	89 (39)[1]	79 (32)
	Effluent	25 (15)	30 (14)
	Removal	72%	62%
TOTAL-P	Influent	4.5 (1.6)	4.0 (1.5)
	Effluent	0.6 (0.3)	1.3 (0.6)
	Removal	86%	69%
FILTERED-P	Influent	3.0 (1.0)	2.6 (1.6)
	Effluent	0.2 (0.1)	.2 (.2)
	Removal	92%	87%
SUSPENDED SOLIDS	Influent	139 (61)	112 (23)
	Effluent	27 (9)	42 (12)
	Removal	81%	62%

[1]Standard deviations

The predominate constituents, other than iron, are zinc and manganese, with the other metals being at least an order of magnitude lower in concentration.

The average concentrations and standard deviations of selected heavy metals encountered in the influent, effluent and sludge from the pilot plant operating at a $Fe_2(SO_4)_3$ addition of 25 mg/l as Fe are

summarized in Table 12.

TABLE 11.

ANALYSIS OF $Fe_2(SO_4)_3$ PRODUCT

COMPONENT	CONCENTRATION	
Total Iron	133	g/l
Cadmium	7.5	mg/l
Chromium	99.3	mg/l
Copper	87.6	mg/l
Lead	22.4	mg/l
Manganese	1.6	g/l
Nickel	4.2	mg/l
Zinc	5.4	g/l

Except for a marginal increase in effluent copper and manganese concentrations, effluent metal levels are the same as, or lower than, the influent raw sewage. Statistical "t" tests on the means revealed that there were no significant differences between influent and effluent concentrations.

Although it is possible that net metal removals through the pilot plant may have been higher if metals were not being added along with the $Fe_2(SO_4)_3$ [i.e., use of pure liquid $Fe_2(SO_4)_3$] it was obvious that there was no net increase in effluent heavy metal loadings. However,

there were high metal concentrations encountered in the sludge (see the third column of Table 12. indicating that the heavy metals added with the $Fe_2(SO_4)_3$ accumulated in the primary sludge. Further, comparison of the

TABLE 12

HEAVY METAL CONCENTRATIONS

IN PILOT PLANT INFLUENT AND EFFLUENT AND SLUDGE

DURING $Fe_2(SO_4)_3$ ADDITIONS

METAL	INFLUENT[1] CONCENTRATION	EFFLUENT[1] CONCENTRATION	SLUDGE CONCENTRATION (mg/1)
Chromium	.014 (.006)[2]	.014 (.004)	7.0 (1.7)
Copper	.062 (.042)	.070 (.051)	14.2 (5.7)
Iron	2.37 (1.41)	2.68 (1.42)	2260 (1320)
Manganese	.323 (.175)	.328 (.198)	8.6 (2.5)
Zinc	.675 (.416)	.570 (.439)	113.6 (45.3)

[1] - Influent and Effluent Concentrations in (mg/1)

[2] - Standard deviations (N = 15) in parentheses

sludge metal concentrations for the two $Fe_2(SO_4)_3$ periods (15 and 25 mg/1) revealed that the increases in sludge metals were somewhat in proportion to the increase in $Fe_2(SO_4)_3$ dosage. For example, zinc, manganese, chromium and copper sludge concentration increases were 56, 36, 35 and 42%,

respectively, in going from the low to higher dose. At the same time, the percent solids of the sludge increased from 1.8 to 2.8% and the total phosphorus from 330 to 1600 mg/l.

Since wastewater and sludge metal concentrations vary greatly depending on municipality (proportion of industrial inputs) and treatment process (conventional settling or lime, $FeCl_3$ or alum assisted settling, as in a phosphorus removal scheme), it is difficult to make comparisons with other sludges. The relatively high metals levels encountered in these sludges may play a role in their disposal (e.g., may prevent disposal on land). Definite conclusions regarding the land disposal of high metal content sludges must await results of the continuing research in this area.

3.5 RESULTS OF FULL-SCALE HEAVY METAL STUDIES AT DUNNVILLE

The means and standard deviations of heavy metals concentrations at various points in the Dunnville Treatment Plant are tabulated in Table 13 (a) for the baseline period and in Table 13 (b) for the pickle liquor addition period. Variations in metal concentrations from sample to sample were quite large as evidenced from the standard deviations. The influent and effluent levels for Cd, As, and Hg were at all times below their respective limits of detectability -- i.e., 1, 5 and 1 µg/l. Due to interferences, arsenic and mercury levels in the pickle liquor could not be quantified, although both were present.

Results on the phosphorus removal aspects of the Dunnville study

TABLE 13

METAL CONCENTRATIONS DURING THE BASELINE AND PICKLE LIQUOR STUDIES AT DUNNVILLE STP

a) BASELINE (Nov. 14, 15, 16, 17, 18, 20 and 21)

SAMPLE[1] LOCATION	Al (µg/l)	Cd (µg/l)	Cr (µg/l)	Cu (µg/l)	Fe (mg/l)	Mn (µg/l)	Ni (µg/l)	Pb (µg/l)	Zn (µg/l)	As (µg/l)	Hg (µg/l)
INFLUENT	681 (616)	<1	15.6 (17.7)	51.9 (21.7)	1.0 (0.8)	78.4 (21.2)	10.3 (5.4)	95.3 (74.4)	164 (231)	<5	<1
EFFLUENT	1248 (138)	<1	6.1 (2.6)	68.6 (64.2)	1.2 (1.6)	74.1 (75.9)	9.8 (6.5)	19.9 (18.7)	173 (121)	<5	<1
AERATION TANK	20.0 (6.7) (mg/l)	28.9 (11.5)	207 (88)	88.6 (13.1)	30.3 (2.9)	820 (155)	100 (57)	571 (205)	1430 (150)	10.3 (2.7)	3.0 (0.0)
AEROBIC DIGESTER	74.1 (9.6) (mg/l)	50.0 (13.7)	224 (150)	103 (19)	81.3 (4.5)	1540 (140)	216 (77)	857 (252)	3030 (143)	15.1 (2.8)	11.7 (2.3)
WASTE SLUDGE	327 (124) (mg/l)	123 (36)	278 (461)	626 (152)	321.6(70.1)	5730 (1480)	572 (432)	724 (874)	10.3 (1.6) (mg/l)	61.4 (22.7)	38.6 (9.0)
DIGESTER SUPERNATANT	730 (509)	3.2 (1.5)	19.3 (7.2)	7.2 (4.2)	1.7 (0.7)	110 (17)	6.2 (7.2)	110 (17)	305 (46)	<5	<1
LAGOON SUPERNATANT	473 (127)	3.8 (1.2)	15.6 (8.0)	4.8 (1.6)	1.6 (0.6)	304 (29)	12.7 (3.1)	49 (12)	101 (54)	<5	<1

(b) PICKLE LIQUOR ADDITION (Feb. 3, 4, 5, 7 and 13)

SAMPLE LOCATION	Al (µg/l)	Cd (µg/l)	Cr (µg/l)	Cu (µg/l)	Fe (mg/l)	Mn (µg/l)	Ni (µg/l)	Pb (µg/l)	Zn (µg/l)	As (µg/l)	Hg (µg/l)
INFLUENT	429 (486)[2]	<1	24.0 (15.6)	102.7(100.2)	1.9 (1.8)	134.5 (72.3)	11.4 (13.2)	84.0 (95.3)	202 (130)	<5	<1
EFFLUENT	538 (1084)	<1	14.2 (17.3)	77.5 (75.6)	4.2 (6.5)	98.1 (70.3)	41.9 (88.6)	48.8 (94.2)	128 (162)	<5	<1
AERATION TANK	11.5 (3.1) (mg/l)	24.3 (32.3)	187 (65)	1130 (240)	214 (70)	1470 (243)	82.1 (88.6)	960 (208)	2790 (321)	16.6 (3.8)	9.0 (0.8)
AEROBIC DIGESTER	31.7 (8.5) (mg/l)	109.0 (70.2)	383 (51)	2120 (236)	487 (55)	2910 (390)	386 (224)	1510 (296)	5460 (468)	29.7 (10.4)	13.9 (3.8)
WASTE SLUDGE	155 (178) (mg/l)	613 (671)	1520 (811)	7050 (1220)	1663 (189)	9450 (1630)	856 (453)	4400 (812)	18600(2650)	77.1 (25.6)	55.7 (15.1)
DIGESTER SUPERNATANT	450 (794)	<1	7.7 (10.8)	55.9 (34.0)	6.2 (7.7)	69.9 (46.4)	13.9 (7.4)	15.4 (12.0)	183 (154)	<5	<1
LAGOON SUPERNATANT	479 (545)	<1	17.0 (9.0)	64.7 (63.2)	11.4(13.5)	227 (117)	12.1 (3.4)	25.0 (21.2)	204 (146)	<5	<1
PICKLE LIQUOR	13.9 (2.1) (mg/l)	1154 (412)	22.6 (2.8) (mg/l)	12.9 (3.1) (mg/l)	108 (3.5) (g/l)	44.0 (34.2) (mg/l)	22.3 (2.7) (mg/l)	5.2 (1.2) (mg/l)	16.4 (12.3) (mg/l)	Interference	Interference

1 -- See Figure 2 for sample locations

2 -- Standard deviations in brackets

have been presented elsewhere (Pollutech Pollution Advisory Services, 1973) and will not be discussed in detail here. In brief, it was found that (i) an effluent phosphorus concentration of less than 1 mg/l would be consistently achieved by a pickle liquor addition of 6-7 mg/l as Fe, and (ii) the pickle liquor addition had no adverse effects on treatment plant performance. Heavy metal aspects are discussed in the following Sections.

3.5.1 Metal Transport Through the Plant

From Tables 13 (a) and (b), it is obvious that there are differences between influent metals levels for the two study periods. Standard statistical "t" tests at the 95% confidence level revealed that influent aluminum was significantly lower during the pickle liquor period and Cr, Cu, Fe, Mn and Ni were significantly higher during the same period, while Pb and Zn levels were essentially unchanged from one period to the other. Because of these inter-period differences, direct comparisons cannot be made of effluent metal levels for the two periods. However, statistical "t" tests applied to the influent and effluent means for the various metals inferred that (i) during the baseline there was some transport of Al through the plant, Cr and Pb were being accumulated in the plant and all other metal levels were virtually unchanged from influent to effluent and (ii) during the pickle liquor addition only iron was transported through the plant, Cr, Mn, Ni and Zn were accumulated and Al, Cu and Pb were unchanged.

A calculation of the relative loading of metals from the pickle liquor to the background (influent) metal loading is made in Table 14.

TABLE 14

CALCULATION OF RELATIVE LOADING OF METALS FROM THE PICKLE LIQUOR ADDITION

	Al	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Conc'n. in Pickle Liquor (mg/l)	13.94	22.64	12.87	108 g/l	44.04	22.31	5.21	16.44
Dosage due to P.L. (µg/l)	.76	1.24	.70	5.90 mg/l	24.05	1.22	.29	.90
Conc'n. in Raw Sewage (µg/l)	429.2	24.00	102.7	1.89 mg/l	13.45	114.3	83.96	202.3
Total Metals Input (µg/l)	430.0	25.24	103.4	7.79 mg/l	158.6	115.5	84.25	203.2
% Load Due to P.L.	.18	4.89	.68	75.75	15.16	1.05	.34	.44

Only in the cases of Cr, Fe, Mn and Ni does the pickle liquor contribute more than 1% of the total metal load. This low loading, coupled with the facts that metals were largely adsorbed onto the mixed liquor solids and that NTA degradation through the plant was good (i.e., average influent and effluent levels over the two study periods were 351 and <25 mg/l, respectively) indicate that the low effluent metal levels

are to be expected. In fact, the effluent levels may have been lower still if it had not been for high suspended solids carry-overs during several days of the two periods. This is further collaborated by the general correlation between effluent metal concentrations and effluent suspended solids. For example, see Figure 11 for the iron-suspended solids relationship. Similar patterns were evident for other metals. In summary, it appears that the pickle liquor additions did not increase effluent metal levels (with the exception of iron) and this is in agreement with the $Fe_2(SO_4)_3$ pilot plant results described in Section 3.4.

3.5.2 Metal Accumulations in the Sludges

As was observed in the $Fe_2(SO_4)_3$ studies, the metals were concentrated in the system sludges. Mixed liquor, aerobic digester, waste sludge (from thickener), lagoon supernatant and digester supernatant metal concentrations are tabulated in Tables 13 (a) and (b). Copper, iron, manganese, lead, and zinc sludge levels were all substantially increased during the pickle liquor additions. Marginal increases in arsenic and mercury were evident. No clear trends for cadmium, chromium or nickel were demonstrated. Return sludge metal concentrations were on the average (for all metals) 2-3 times higher than the mixed liquor solids. This was as expected since the average ratio of return sludge to mixed liquor sludge suspended solids was 7300/2650 or 2.7:1.

Concentration factors for the various metals are summarized in Table 15. Concentration factors for the influent to mixed liquor, the

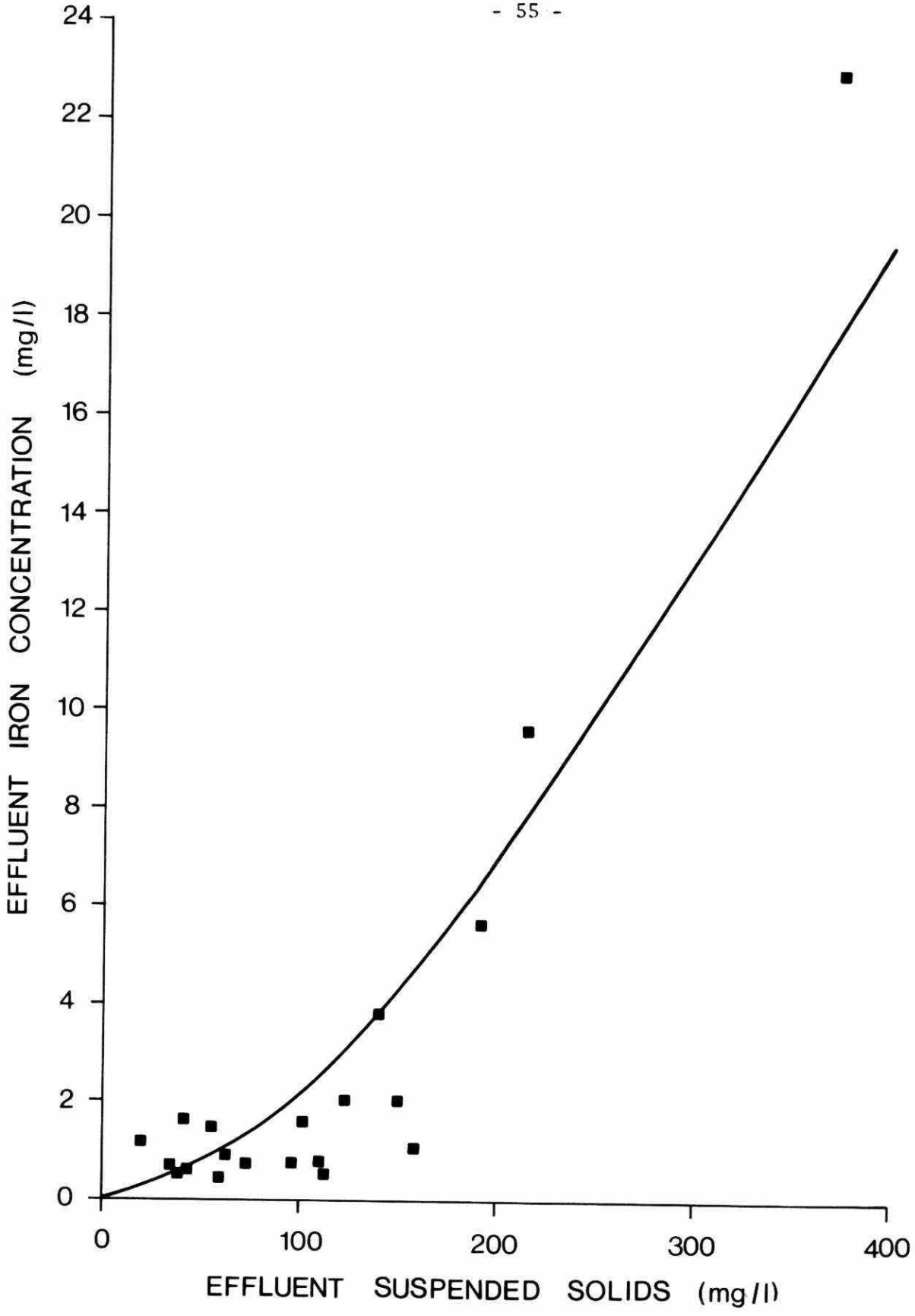


FIGURE 11 : RELATIONSHIP BETWEEN EFFLUENT IRON CONCENTRATION AND SUSPENDED SOLIDS

mixed liquor to aerobic digester and aerobic digester to waste sludge were calculated for the two periods from the relative metals concentrations in the various streams.

TABLE 15

METAL CONCENTRATION FACTORS THROUGH THE DUNNVILLE PLANT

		Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	As	Hg	SUSPENDED SOLIDS
Mixed Liquor Influent	BL[1]	29	--	13	2	30	11	10	6	9	--	--	--
	PL[2]	27	--	8	11	113	11	7	11	14	--	--	--
Aerobic Digester Mixed Liquor	BL	3.7	1.7	1.1	1.2	2.7	1.9	2.2	1.5	2.1	1.5	3.9	2.4
	PL	2.7	4.5	2.0	1.9	2.3	2.0	4.7	1.6	2.0	1.8	1.5	2.7
Waste Sludge Aerobic Digester	BL	4.4	2.5	1.2	6.1	4.0	3.7	2.6	1.0	3.4	4.1	3.3	3.2
	PL	4.9	5.6	4.0	3.3	3.4	3.3	2.2	2.9	3.4	2.6	4.0	3.3

[1] -- Baseline

[2] -- Pickle Liquor

The concentration factors from influent to mixed liquor are highest and appear to be dependent on the metal being considered with aluminum

and iron being more concentrated than the other metals. Although there is variability in the aerobic digester/mixed liquor and waste sludge/aerobic digester concentration factors, it appears that, overall, the effect is physical (i.e., concentration of solids -- note suspended solids ratios in the last column of Table 15 and compare to the concentration factors for the various metals).

In general, metal levels in the digester and lagoon supernatants were low and in the same order as the raw sewage levels. This indicates that there was very little resolubilization of metals from the sludges in the aerobic digester or lagoon. Cd, Cr, Mn and Pb supernatant concentrations were lower during the pickle liquor period, Cu, and Fe were higher and no clear trends were evident for aluminum, arsenic or mercury.

The results of the Dunnville study show that pickle liquor additions will not significantly increase effluent metal loadings; however, metal levels in sludges are substantially increased and this may influence the ultimate disposal of these sludges.

BIBLIOGRAPHY

Abbott, R.A., Metals in Municipal Sewerage Systems, Ontario Water Resources Commission (1971)

APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, Thirteenth Ed. (1971)

Bjorndal, H., Bouveng, H.O., Solyon, P., and Werner, J., NTA in Sewage Treatment, Vatten 28, (1) :5 (1972)

Canadian Trade Index, Canadian Manufacturers' Association (1971)

Cousins, W.G., Some Aspects of Toxicity of Metal Ions to Sewage Treatment Processes; Ontario Water Resources Commission (1960)

Dempter, J. H., and Gomaa; Recovery and Recycle of Waste Acid from Steel Pickling Operations; Paper presented at the Annual Convention of the Wire Association (1972)

Detroit Metro Water Department, Development of Phosphate Removal Processes, WPCRS 17010 FAH 07/70 (1970)

Fraser's Canadian Trade Directory, 59th Edition (1972)

Harvard University, Oxygenation of Ferrous Iron, WPCRS 14010 06/69 (1970)

Jenkins, D, Ferguson, J. F., and Menar, A. B.; Chemical Processes for Phosphate Removal; Water Research 5 (7) :369 (1971)

Jenkins, S.H., and Hewitt, C.H., The Effect of Chromium Compounds on the Purification of Sewage by the Activated Sludge Process, J. & Proc. Int. Sew. Purif. (1942)

Jones, H. R., Detergents and Pollution; Pollution Control Review #7, Noyes Data Corporation (1972)

Ontario Water Resources Commission, Industrial Waste Survey, County of Welland; Industrial Wastes Branch (1964)

Pearse, L. et al, "Chemical Treatment of Sewage"; Sewage Works Journal, 7 (6) :997 (1935)

Pollutech Pollution Advisory Services, Personal Communication, (1973)

Prince, A.T., and Bruce, J.P., Development of Nutrient Control Policies in Canada; Department of the Environment, Inland Waters Branch, Technical Report #51 (1972)

Rand Development Corporation, Phosphorus Removal Using Ferrous Iron and Lime, WPCRS 11010 EGO 01/71 (1971)

Scott, D. S., Use and Production of Iron Salts for Phosphorus Removal, Canada-Ontario Agreement on Great Lakes Water Quality, Research Report No. 5, (1973)

Sewerage Commission of the City of Milwaukee, Phosphorus Removal with Pickle Liquor from an Activated Sludge Plant, WPCRS 11010 FLQ 03/71 (1971)

Traversy, W. J., Methods for Chemical Analysis of Waters and Wastewaters; Water Quality Division, Dept. of Fisheries and Forestry, Ottawa (1971)

Verghese, K. I., Personal communication (1973)

Wilms, D. A., Notebaert, F. F., and Van Hante, A. A.; Removal of Chromates from Pickling Liquors by Adsorption of Hydrous Ferric Oxide; Presented at the 6th International Water Pollution Research Conference, Jerusalem (1972)

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APPENDIX A

LIST OF COMPANIES CONTACTED

AND

LETTER SENT TO COMPANIES

APPENDIX A

A.1 (1)

COMPANIES CONTACTED	TYPE OF WASTE PRODUCT
Masterloy Products Ltd. - Ottawa, Ontario	O
Metals and Alloys Co. Ltd. - Toronto, Ontario	O
St. Clair Chemicals Ltd. - Mississauga, Ontario	
Welland Iron and Brass Ltd. - Welland, Ontario	
Canbro Div'n. of Int. Bronze Powders Ltd. - Valleyfield, Quebec	
Canadian Carborundum Ltd. - Niagara Falls, Ontario	
Aluminum Reduction Co. - Concord, Ontario	
Aluminum Company of Canada Ltd. - Montreal, Quebec	RM
Aluminum Foundry and Pattern Works Ltd. - Montreal, Quebec	
Alumalloy Castings Ltd. - Montreal, Quebec	
Aluminum Permanent Mould - Waterloo, Quebec	
Alumicor Ltd. - Scarborough, Ontario	
General Smelting of Canada Ltd. - Burlington, Ontario	
H. Bernard (Canada) Ltd. - West Hill, Ontario	
Atlas Steels Co. - Welland, Ontario	PL
The Algoma Steel Corp. Ltd. - Sault Ste. Marie, Ontario	PL, MS
Atlas Alloys Ltd. - Toronto, Ontario	
Dominion Steel and Coal Ltd. - Montreal, Quebec	
Rio Algom Mines Ltd. - Toronto, Ontario	
Stanley Steel Company Ltd. - Hamilton, Ontario	
Union Drawn Steel Co. - Hamilton, Ontario	
Burlington Steel Co. - Hamilton, Ontario	MS, BHD, SL
Nichols Chemical Co. Ltd. - Thorold, Ontario	
The Norton Company, Chippawa, Ontario	O
Dominion Chain Co. - Stratford, Ontario	
Page-Hershey Tubes Ltd. - Welland, Ontario	
The P. L. Robertson Co. Ltd. - Milton, Ontario	O
Algoma Steel Corp., Canadian Furnaces Div'n., Port Colborne Ontario	
(1) -- See Legend at End of Table	

COMPANIES CONTACTED	TYPE OF WASTE PRODUCT
Lang Manufacturing Division, Borg-Warner (Canada) Ltd. - Oakville, Ontario	
Fahralloy Canada Ltd. - Orillia, Ontario	
Baycoat Ltd. - Hamilton, Ontario	
Domtar Ltd. - Montreal, Quebec	CL
Fina Metal Industries, Petrafina Canada - Pointe aux Trembles, Quebec	O
North American Rockwell Ltd. - Chatham, Ontario	PL
Indian Steel Products of Canada Ltd. - Kitchener, Ontario	SL
Dahmer Steel Ltd. - Kitchener, Ontario	SL
Eastern Steel Products - Preston, Ontario	
Etobicoke Iron Works - Weston, Ontario	
Presland Iron and Steel Works - Kingston, Ontario	
Dynamic Industries Inc. - Quebec, Quebec	
Leeds Bridge and Iron Works - Gananoque, Ontario	
Simonds Canada Saw Division - Granby, Quebec	
Reynolds Aluminum Co. of Canada Ltd. - Montreal, Quebec	DR
Kaiser Aluminum Co., Scarborough, Ontario	
Noranda Metal Industries Ltd. - Montreal, Quebec	
Noranda Mines Ltd. - Toronto, Ontario	O
National Steel Car Corp. Ltd. - Hamilton, Ontario	
National Steel Drum Ltd. - Petrolia, Ontario	O
Rheem Canada Ltd. - Hamilton, Ontario	
Rock Drill Rod Co. Ltd. - Malton, Ontario	
G and H Steel Service of Canada Ltd. - Scarborough, Ontario	
Dominion Engineering Works Ltd. - Montreal, Quebec	
Forano Ltd. - Plessisville, Quebec	
J. A. Gosselin Co. Ltd. - Drummondville, Quebec	
Port Arthur Shipbuilding Co. - Thunder Bay, Ontario	
Canadian Shipbuilding and Engineering Ltd. - Collingwood, Ont.	
Canadian Metal Rolling Mills - Mississauga, Ontario	
Central Bridge Division of the Toronto Iron Works - Toronto, Ontario	CL

COMPANIES CONTACTED	TYPE OF WASTE PRODUCT
Canadian Vickers Ltd. - Montreal, Quebec	
Volcano Ltd. - Montreal, Quebec	
Canada Forgings Ltd. - Welland, Ontario	MS
Interlake Steel Products Co., Ltd. - Thorold, Ontario	PL
Mills Steel Products Ltd. - Hamilton, Ontario	
Griffin Steel Foundries - Ste. Hyacinthe, Quebec	SL
Continental Can Co. of Canada Ltd. - Toronto, Ontario	
Wire Rope Industries of Canada Ltd. - Montreal, Quebec	
Molybdenite Corporation of Canada Ltd. - Montreal, Quebec	
King Calcium Products Ltd. - Campbellville, Ontario	
Canada Cement Laforge Ltd. - Montreal, Quebec	SPD
The Canada Metal Co. Ltd. - Toronto, Ontario	SL, O
Canada Valve Ltd. - Kitchener, Ontario	
Canada Wire and Cable Co. Ltd. - Toronto, Ontario	
Canadian Acme Screw and Gear Ltd. - Toronto, Ontario	
Canadian Bronze Company Ltd. - Montreal, Quebec	
Dominion Foundries & Steel Ltd. - Hamilton, Ontario	PL, SL, BHD
Dominion Forge Co. - Windsor, Ontario	MS
Canadian Steel Foundries Ltd. - Montreal, Quebec	
Perth Metal Industries Ltd. - Stratford, Ontario	
General Wire and Cable Co. - Cobourg, Ontario	
Union Carbide Canada Ltd. - Toronto, Ontario	CL
Welmet Industries Ltd. - Welland, Ontario	MS
Lake Ontario Steel Co. - Whitby, Ontario	
Reinforcing Steel Products Co. - Toronto, Ontario	
Structural Inc. - Quebec, Quebec	
York Steel Construction Ltd. - Toronto, Ontario	
Thompson-Gordon Ltd. - Hamilton, Ontario	
Canadian SKF Co. Ltd. - Scarborough, Ontario	O
The Steel Company of Canada Ltd. - Hamilton, Ontario	BHD, O
Link-Belt Ltd. - Scarborough, Ontario	

COMPANIES CONTACTED	TYPE OF WASTE PRODUCT
The Torrington Co. Ltd. - Bedford, Quebec	
Babcock & Wilcox Canada Ltd. - Cambridge, Ontario	
Canadian Oxygen Ltd. - Toronto, Ontario	CL
National Oxygen Ltd. - Oakville, Ontario	
Canadian Johns-Manville Co. Ltd. - Port Credit, Ontario	
Lake Ontario Cement Ltd. - Toronto, Ontario	SPD
Reynolds Extrusion Co. - Richmond Hill, Ontario	DR
Canadian Liquid Air Ltd. - Montreal, Quebec	CL
Canadian Hanson & Van Winkle Ltd. - Toronto, Ontario	
Federated Metals Canada Ltd. - Scarborough, Ontario	
George White and Sons Ltd. - London, Ontario	
East Side Plating (Canada) Ltd. - Windsor, Ontario	PL
Motor Wheel Industries - Chatham, Ontario	
Peace River Mining and Smelting Ltd. - Amherstburg, Ontario	
Dosco Ltd. - Etobicoke, Ontario	F
Liquid Carbonic Canadian Corp. Ltd. - Montreal, Quebec	CL
Ford Motor Company of Canada Ltd. - Oakville, Ontario	O
General Motors of Canada Ltd. - Oshawa, Ontario	O
American Motors (Canada) Ltd. - Brampton, Ontario	
The Wabi Iron Works Ltd. - New Liskeard, Ontario	
Quebec Iron Foundries Ltd. - Noranda, Quebec	
Industrial Containers Ltd. - LaSalle, Quebec	
Avco Bay State, Canada, Ltd. - Brantford, Ontario	
Canadian Heat Treaters Ltd. - Richmond Hill, Ontario	
Brunner and Lay (Canada) Ltd. - Lachine, Quebec	
Jessop Steel of Canada Ltd. - Wallaceburg, Ontario	
Simonds Canada Abrasive Division, Arvida, Quebec	O
Minnesota Mining and Manufacturing Ltd. - London, Ontario	
Chromasco Corp. - Montreal, Quebec	O
Admiral Sanitation Ltd. - Scarborough, Ontario	
Mallory Battery Co. of Canada Ltd. - Mississauga, Ontario	
Canadian Gypsum Ltd. - Toronto, Ontario	

COMPANIES CONTACTED	TYPE OF WASTE PRODUCT
Acadian Platers Co. Ltd. - Rexdale, Ontario	
Accurate Machine and Tool Ltd. - Weston, Ontario	
Anti-Friction Enterprises Ltd. - Rexdale, Ontario	
Associated Tube Industries Ltd. - Milliken, Ontario	
Bombardier Ltd. - Shefford, Quebec	O
Cametoid Ltd. - Ajax, Ontario	
Galt British Forge Ltd. - Cambridge, Ontario	MS
Karemchemie Corp. - Toronto, Ontario	F
Electric Reduction Co. - Toronto, Ontario	
Lundy Steel Products - Dunnville, Ontario	PL, O
Firestone Steel Products - London, Ontario	F
Canadian Titanium Dioxide Pigments - Montreal, Quebec	SA
Federated Genco Ltd. - Burlington, Ontario	
Burlington Die Casting Ltd. - Burlington, Ontario	DR
Arthur Balfour and Co. (Canada) Ltd. - Montreal, Quebec	
Colt Industries (Canada) Ltd. - Sorel, Quebec	
Dominion Bridge Ltd. - Montreal, Quebec	
Borg-Warner (Canada) Ltd. - Arvida, Quebec	

LEGEND

MS = Mill Scale
PL = Pickle Liquor
F = Reclaimed $FeSO_4.7H_2O$
SA = Spent Mine Acid
CL = Carbide Lime
SPD = Stack Precipitator Dust
BHD = Bag House Dust
RM = Red Mud
DR = Dross
SL = Slag
O = Other Waste Products

A.2

LETTER SENT TO THE COMPANIES

Canada Centre for Inland Waters,
Wastewater Technology Centre,
Environmental Protection Service,
867 Lakeshore Road,
P. O. Box 5050,
Burlington, Ontario.

_____

_____

_____

Dear Sir:

The Environmental Protection Service at the Canada Centre for Inland Waters has initiated a project to investigate the usefulness of industrial wastes for the removal of phosphorus from municipal sewage.

Phosphorus can be chemically precipitated by treatment with iron, aluminum and calcium compounds under appropriate pH conditions. The usual chemicals employed are ferrous and ferric chloride, alum, sodium aluminate, slaked lime and calcium oxide. Our studies are to determine which wastes or combinations of wastes would be useful to achieve phosphorus removal. Any wastes in solid or liquid form containing significant quantities of iron, aluminum or calcium, acid or alkali may be of some use. Spent pickling solutions, waste lime or aluminum products are obvious examples.

We would be interested in including any appropriate wastes from your operations in this study. This would involve us receiving a few pounds of waste sample within the next few weeks and two or three additional samples over the next few months. This will allow us to examine its usefulness and variability. If necessary, we could arrange to pay the shipping costs of the samples. Please let us know if you have any such wastes and when we could arrange to obtain the first sample. Any information about composition and origin of the waste would be helpful.

Your co-operation in this study will be greatly appreciated.

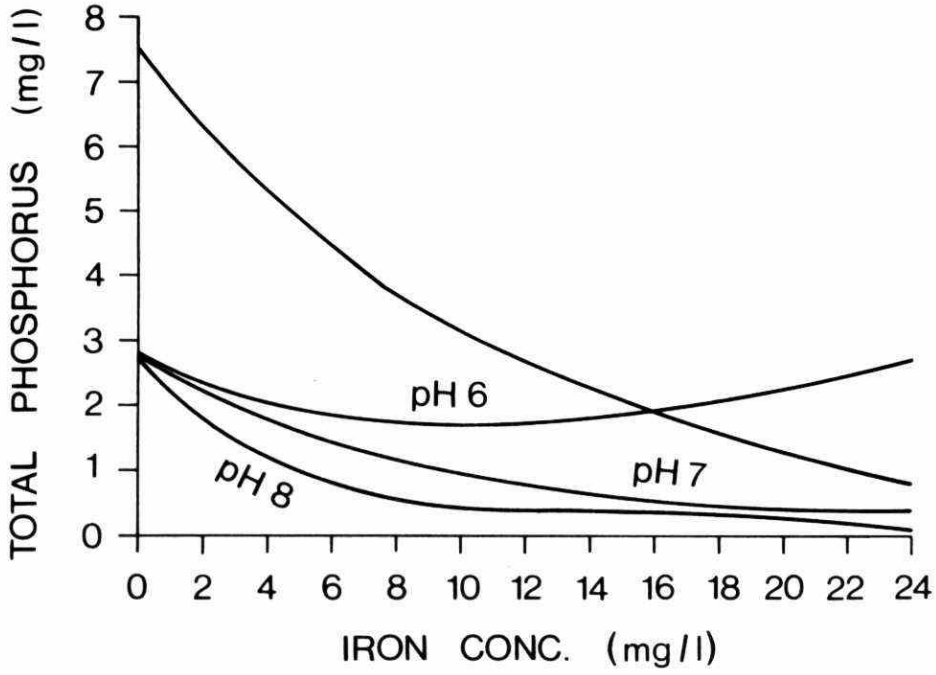
Yours truly,

Peter Fowlie,
Process Development Chemist.

APPENDIX B

JAR TEST RESULTS
FOR
SELECTED WASTE MATERIALS

NOTE: The Figures in this Appendix are presented according to a standard format where (i) the portion of the Figure on the left presents the results of several individual jar tests performed with the indicated material on Skyway raw sewage and (ii) the portion of the Figure on the right indicates the effect of pH on phosphorus removal for one particular dosage level of the material.



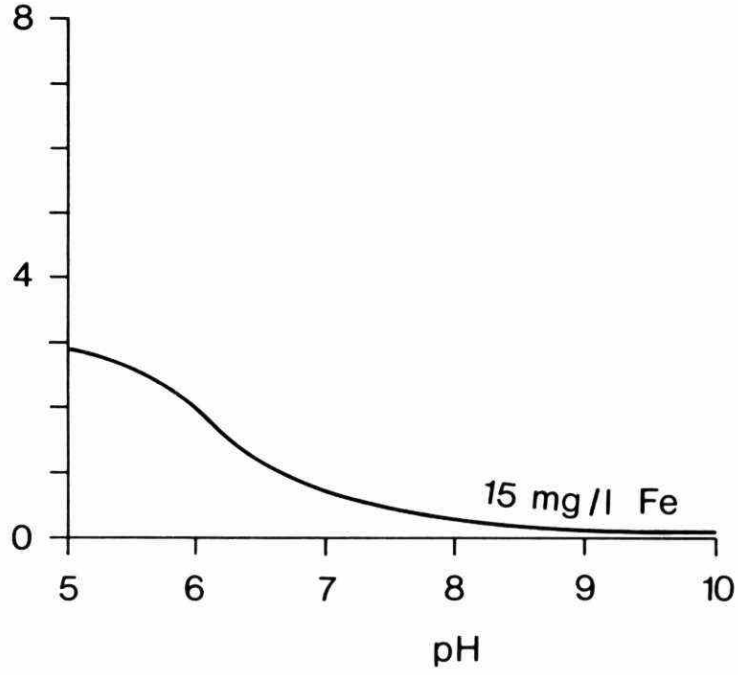
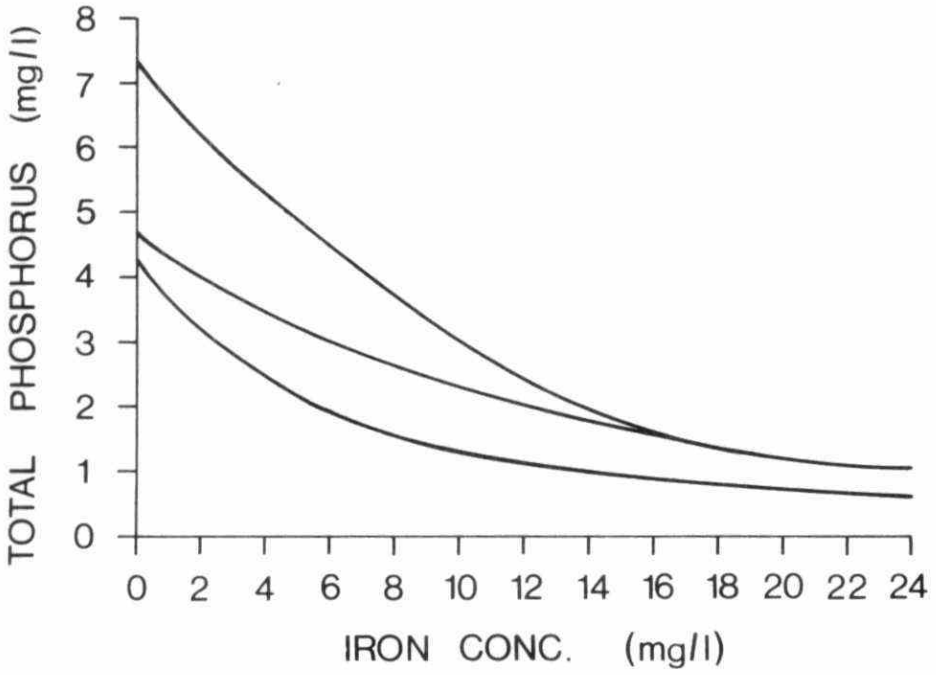


FIGURE B-1 : ATLAS STEEL CO. - PICKLE LIQUOR



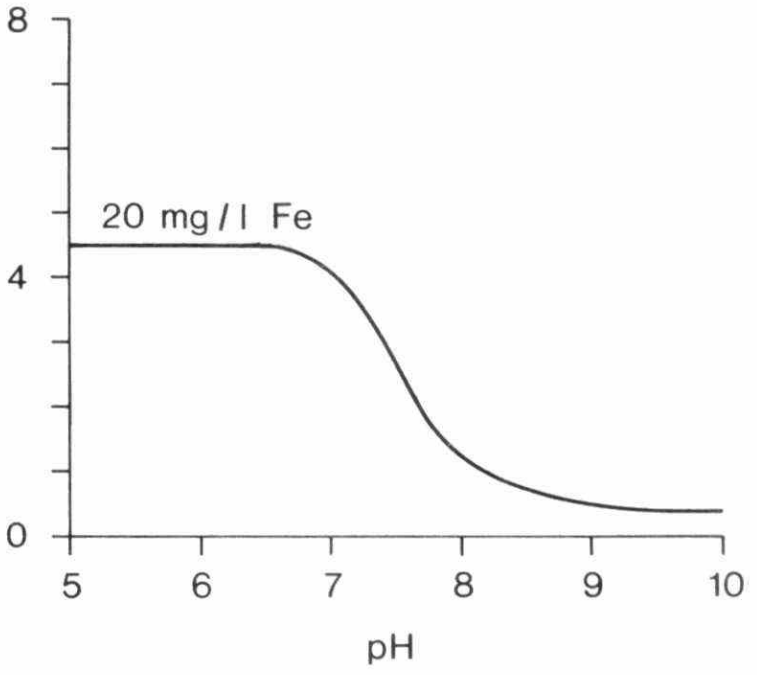
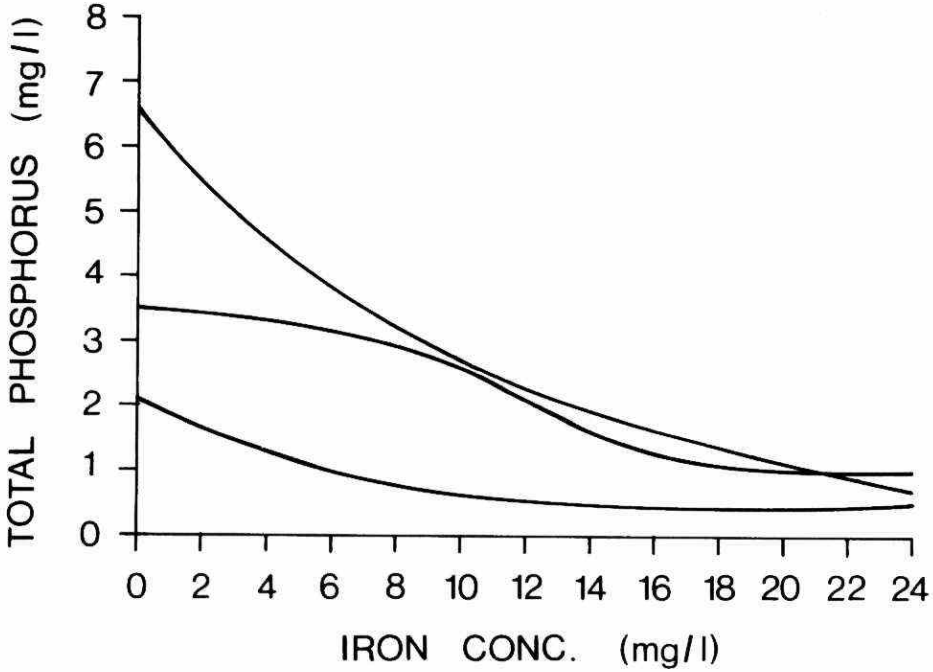


FIGURE B - 2 : ALGOMA STEEL CORP. - PICKLE LIQUOR



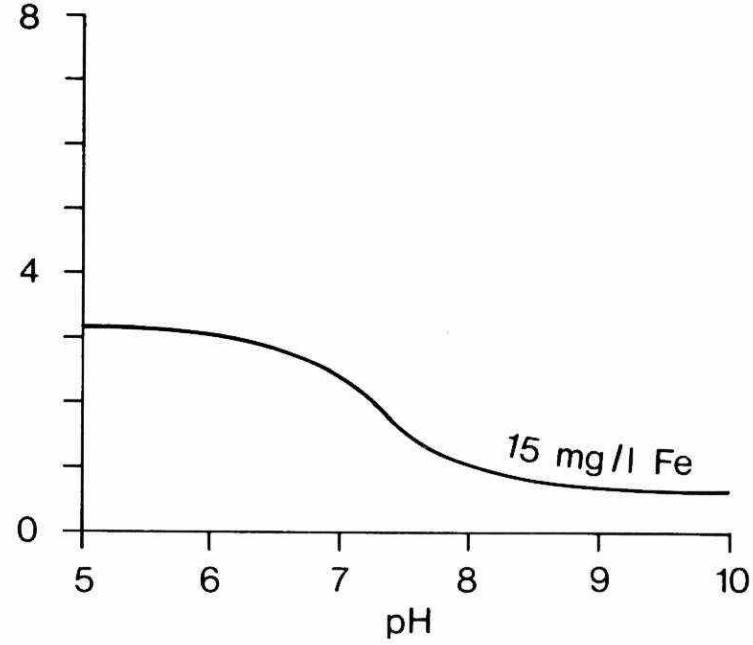
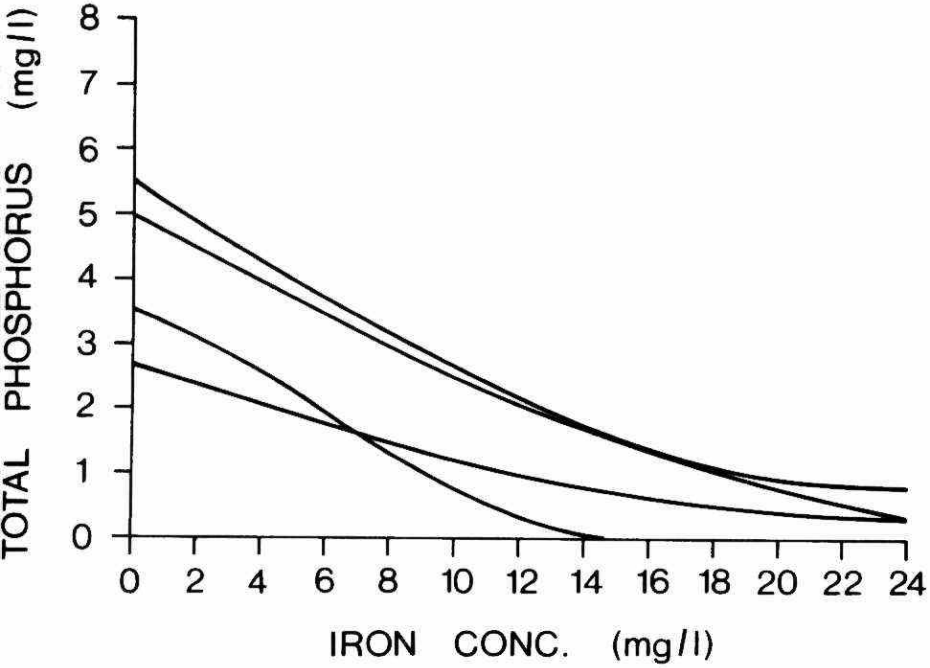


FIGURE B - 3 : ATLAS STEEL CO. - HNO_3 / HF PICKLE LIQUOR



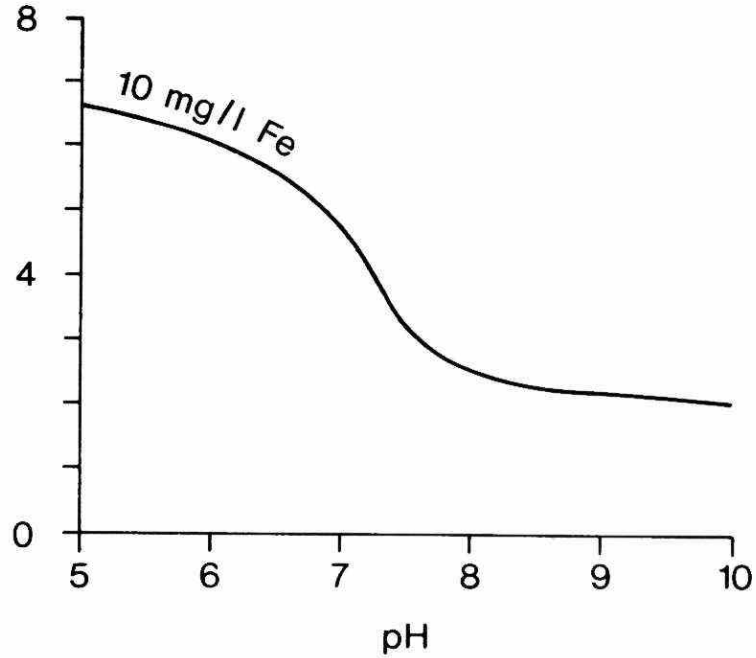
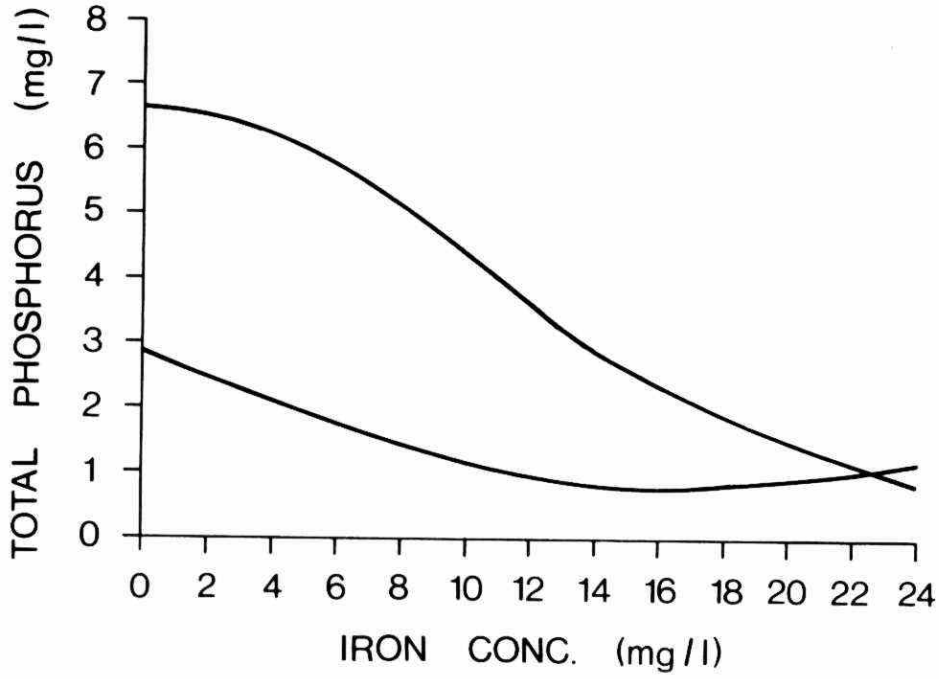


FIGURE B - 4 : NORTH AMERICAN ROCKWELL - PICKLE LIQUOR



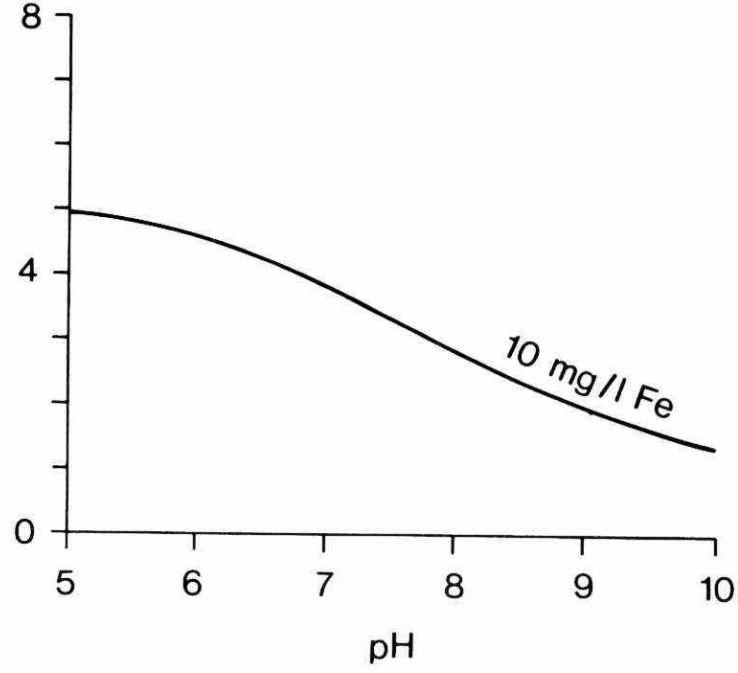
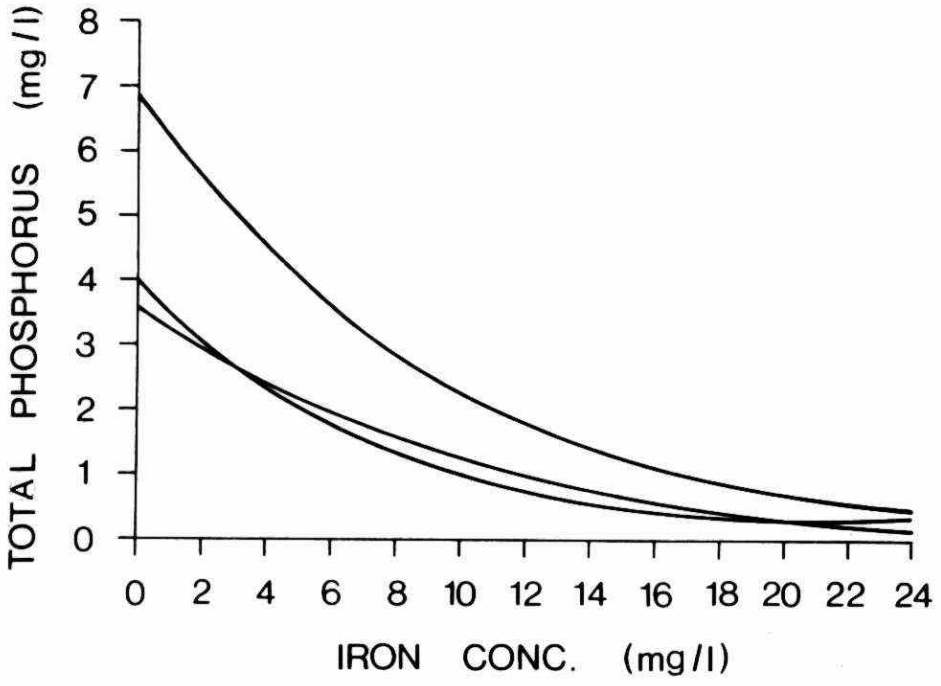


FIGURE B-5 : INTERLAKE STEEL CO. - PICKLE LIQUOR



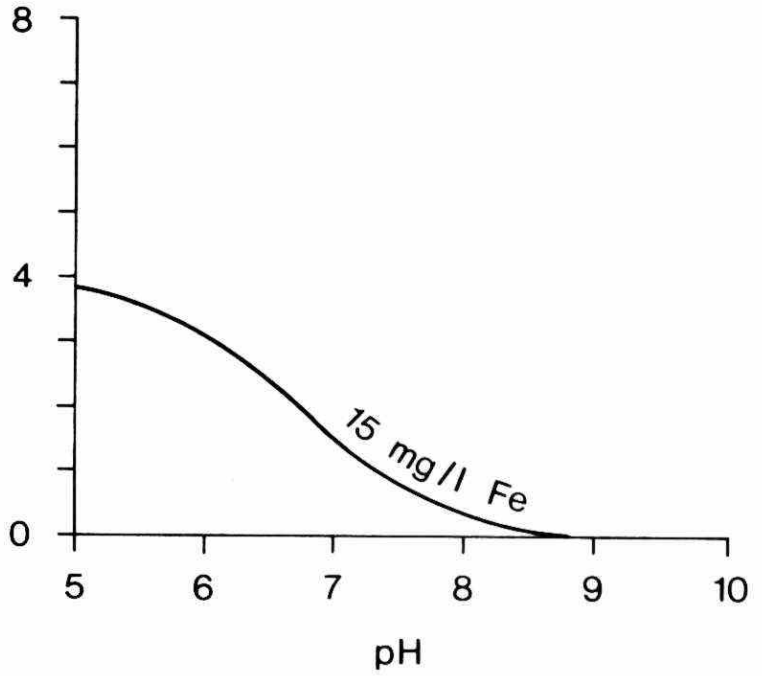
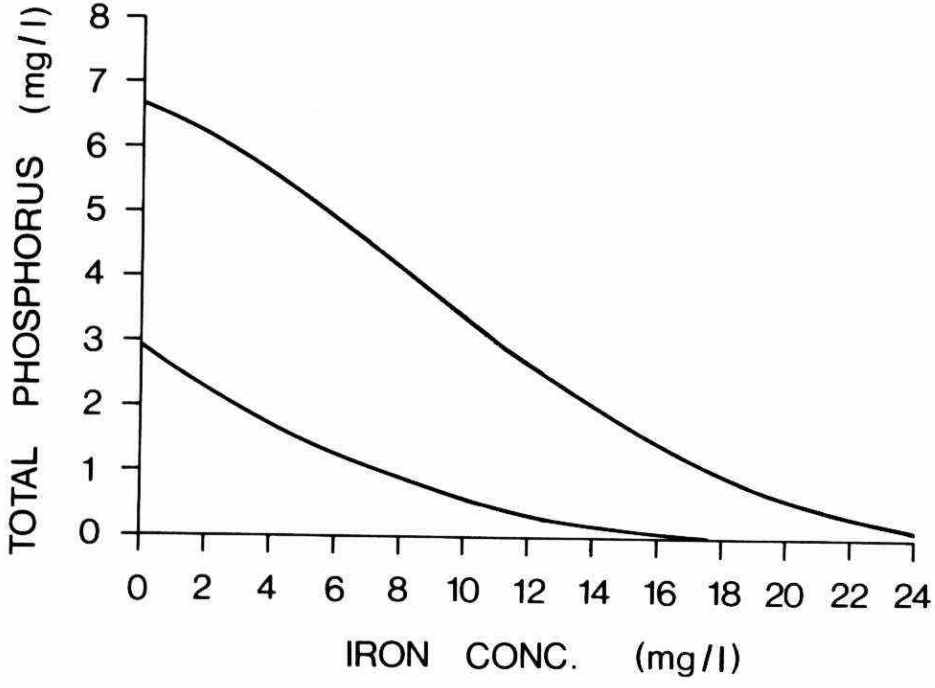


FIGURE B – 6 : LUNDY STEEL PRODUCTS – PICKLE LIQUOR



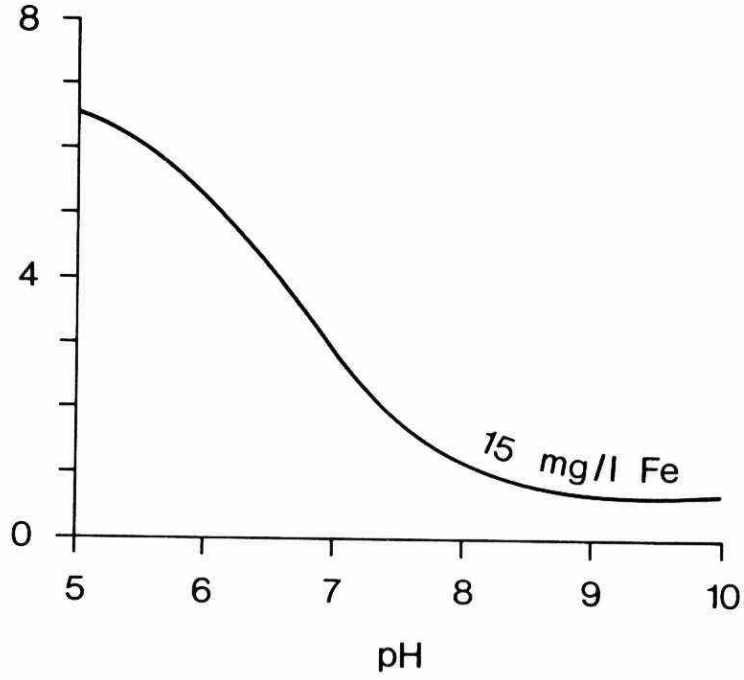
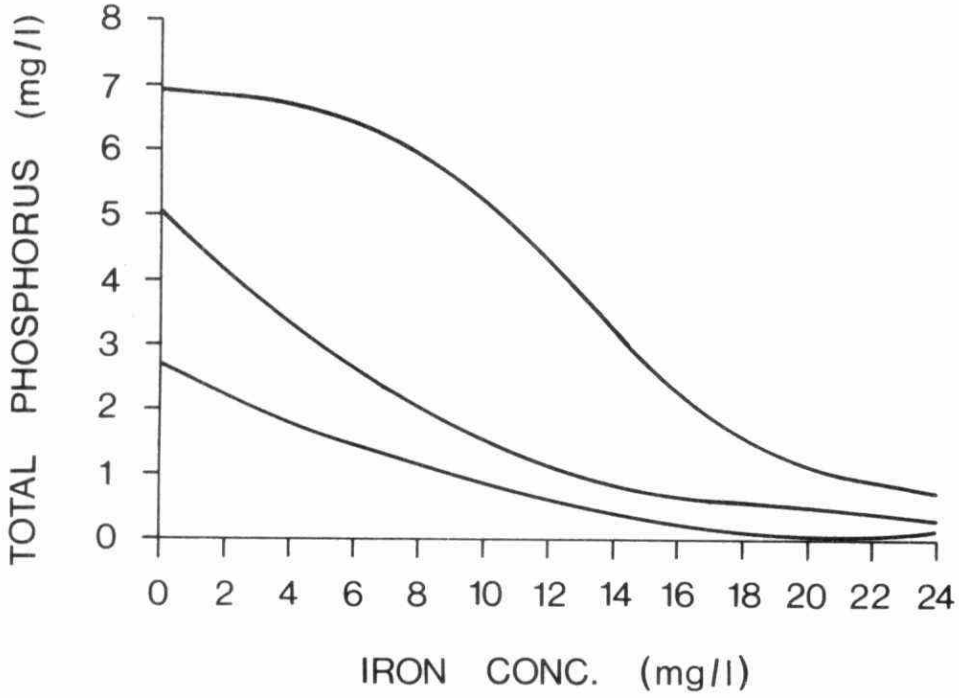


FIGURE B – 7 : EAST SIDE PLATING – PICKLE LIQUOR



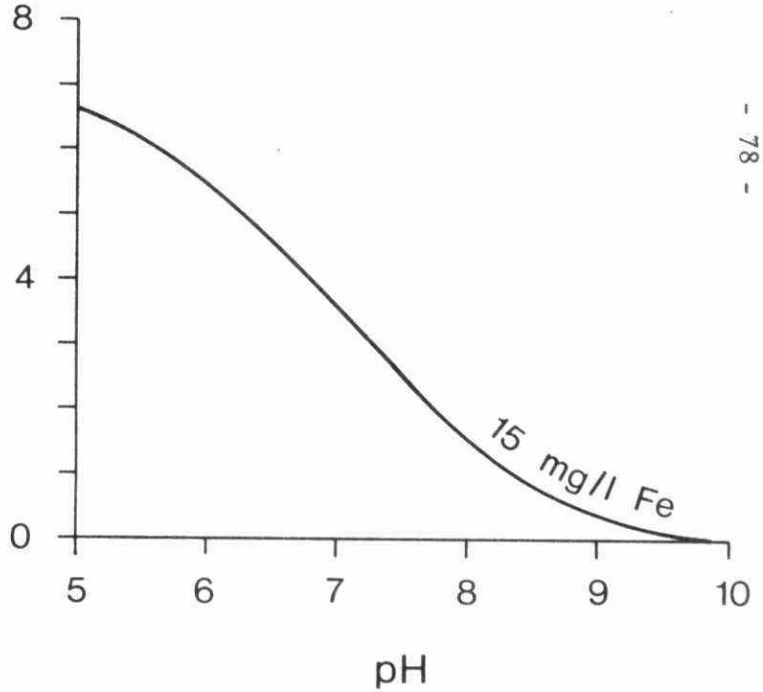
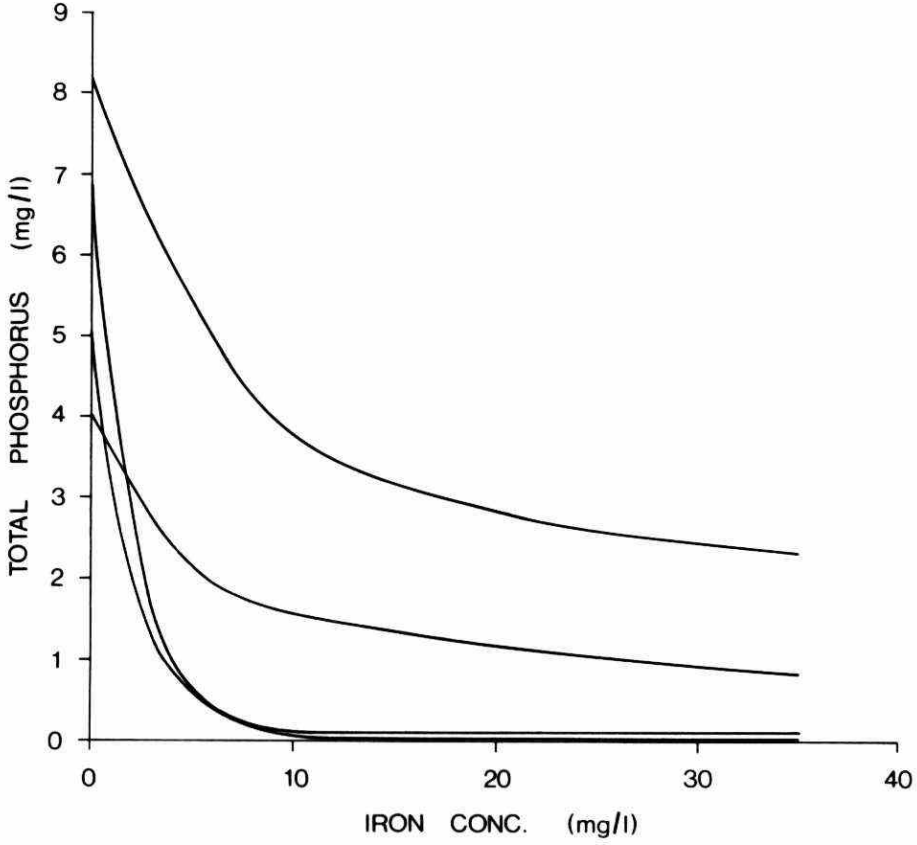


FIGURE B - 8 : DOFASCO - PICKLE LIQUOR



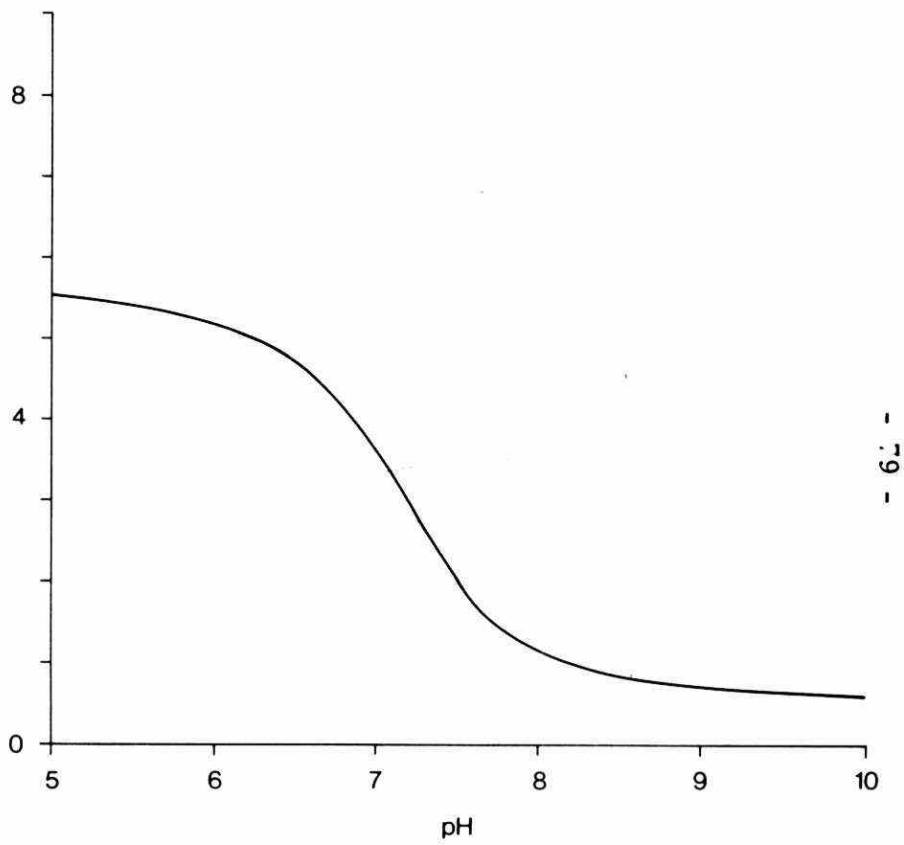
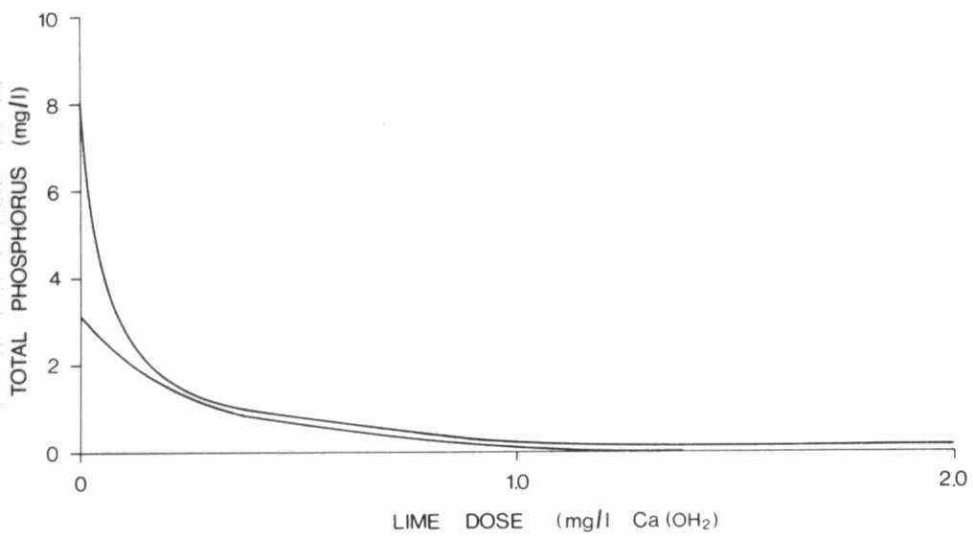


FIGURE B – 9 : KAREMCHEMIE – $Fe \cdot SO_4$



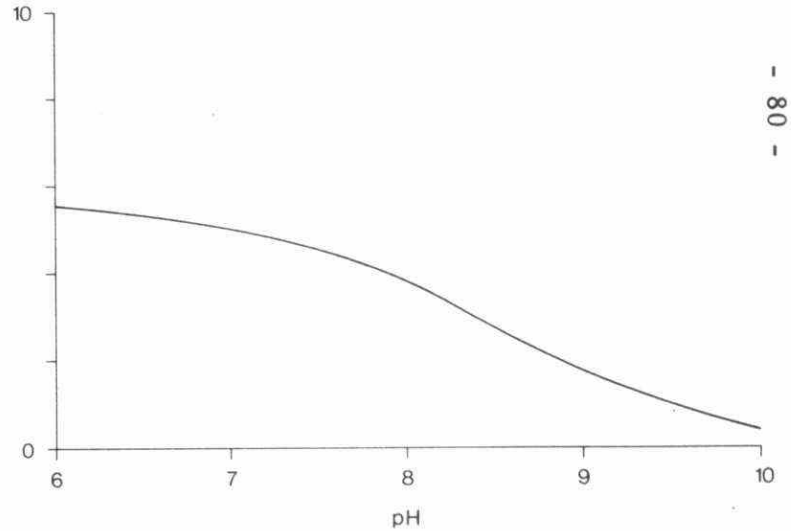
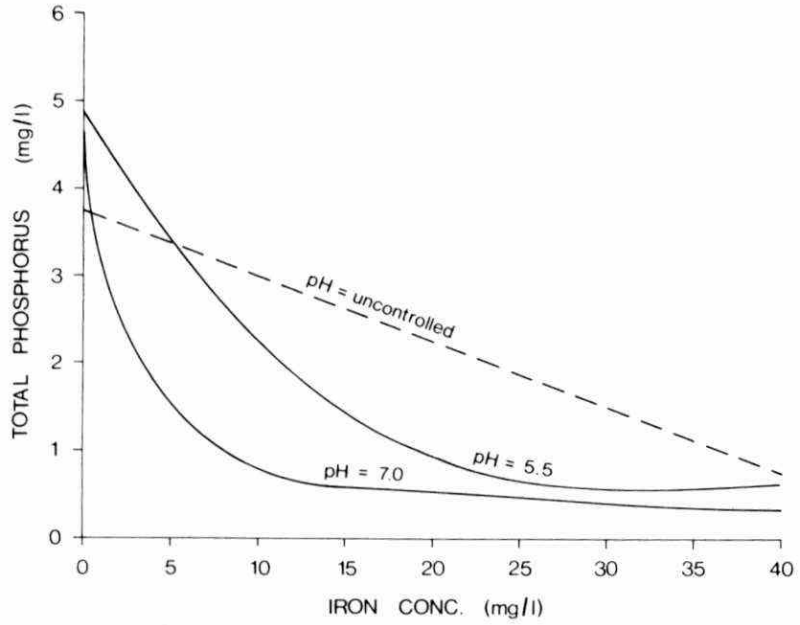


FIGURE B - 10 : CANADIAN OXYGEN LTD. - CARBIDE LIME



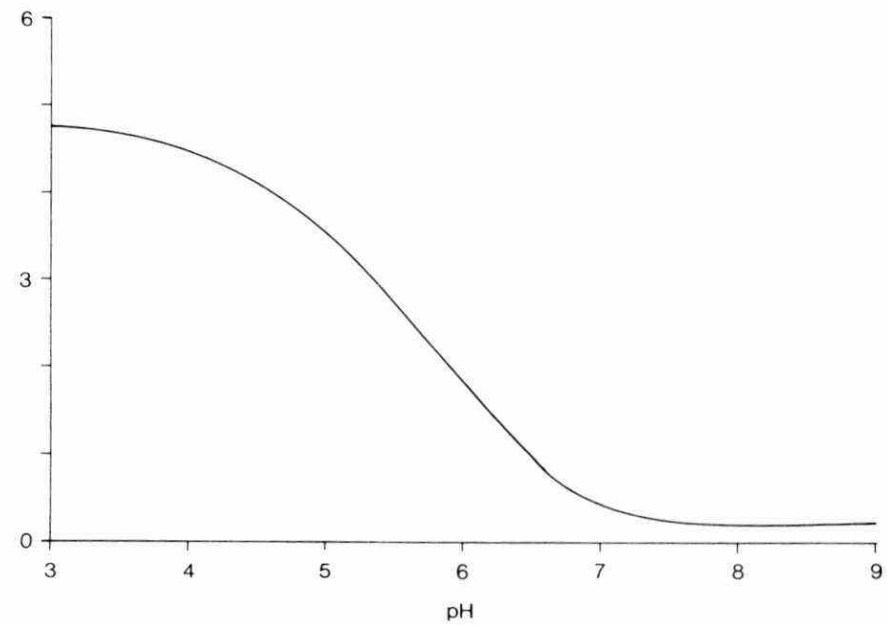
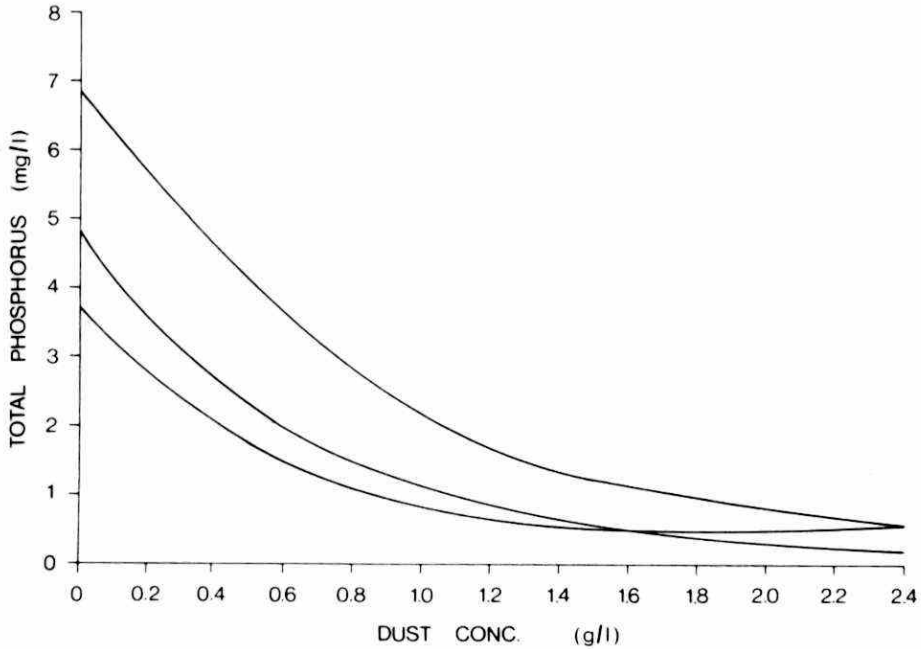


FIGURE B – 11: CANADIAN TITANIUM DIOXIDE PIGMENTS – SPENT ACID



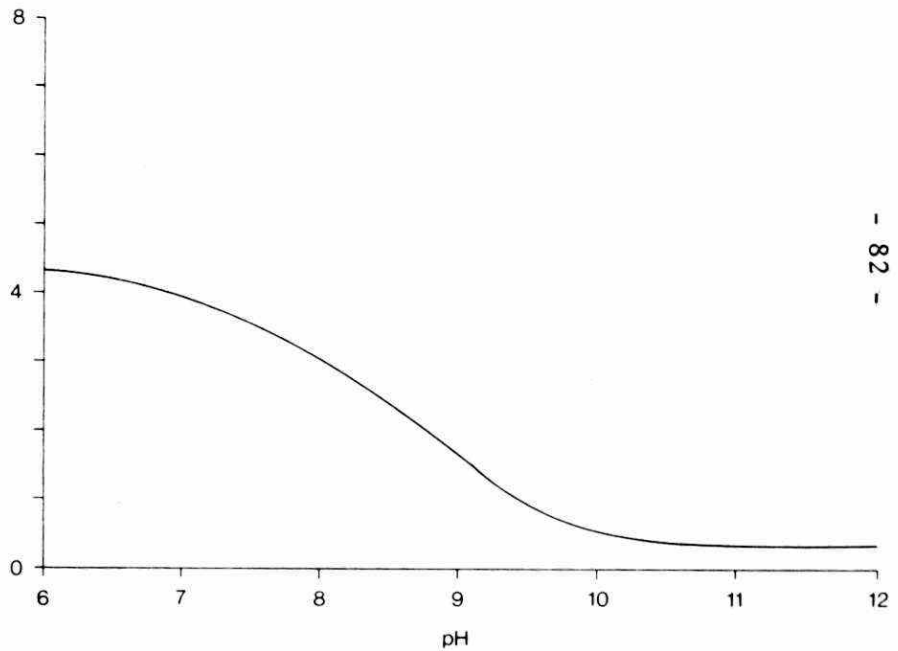
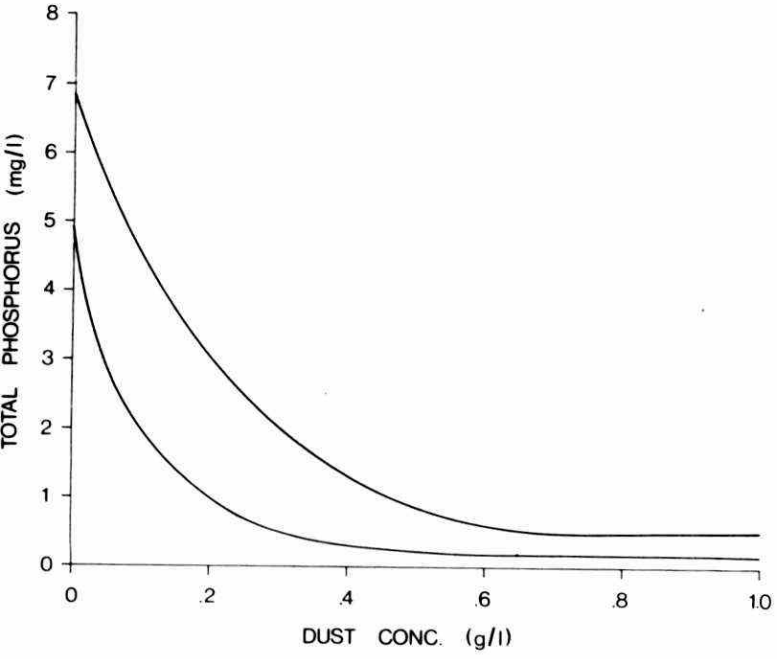


FIGURE B – 12 : LAKE ONTARIO CEMENT. STACK – PRECIPITATOR DUST



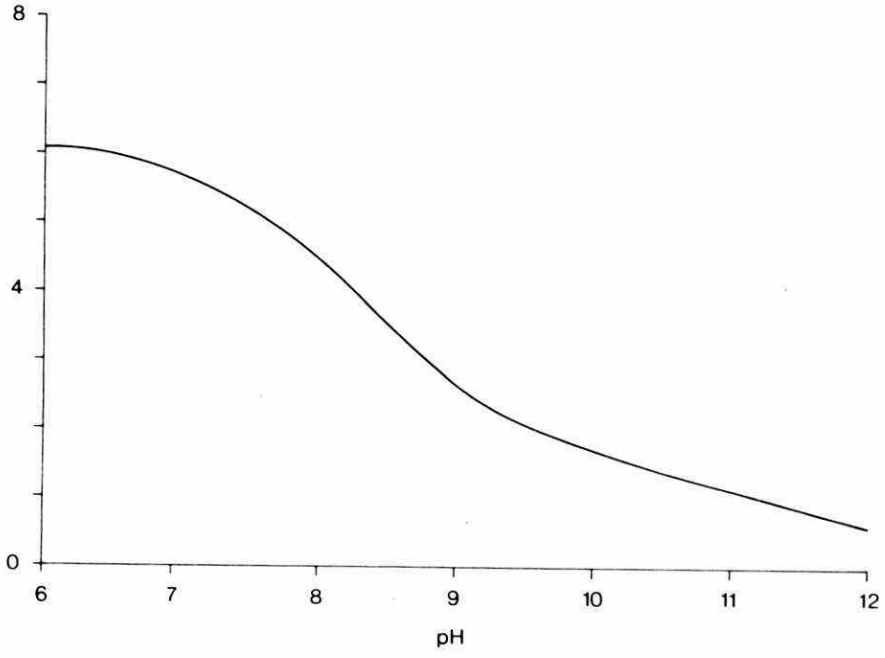


FIGURE B - 13 : STELCO - BAGHOUSE DUST

APPENDIX C

ANALYTICAL PROCEDURES

APPENDIX C

ANALYTICAL PROCEDURES

Arsenic

Arsenic was determined according to Traversy (1971) by a method whereby arsenic is reduced to arsine (AsH_3) by zinc in acid solution. The arsine is passed through a scrubber containing glass wool impregnated with lead acetate solution and into an absorber tube containing silver diethyldithiocarbonate dissolved in pyridine. The arsenic reacts with the silver salt to form a red complex suitable for colourimetric measurement.

Chemical Oxygen Demand (COD)

COD was determined by Standard Methods (1971). Organics and other oxidizable substances in the sample were oxidized by refluxing in a mixture of sulfuric acid and potassium dichromate in known quantities. Excess dichromate was titrated with ferrous ammonium sulfate.

Heavy Metals

The samples taken for heavy metal analyses (Al, Ca, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) were digested in boiling aqua regia (10 ml HCL + 3 ml HNO_3 per 250 ml of water sample, 20 ml HCL + 6 ml HNO_3 per 250 ml sludge sample) to dryness. Any residual organic material was oxidized with a few drops of 30% H_2O_2. The individual metals were then determined according to Traversy (1971) by atomic absorption.

Mercury

Samples taken for mercury analysis were immediately acidified with 1 ml conc. H_2SO_4 per 500 ml sample to prevent loss by evaporation. The mercury was determined by an automated atomic absorption procedure described by Traversy (1971).

Nitrilotriacetic Acid (NTA)

Since NTA is a biodegradable compound, samples for this analysis were immediately preserved in 0.5% formaldehyde and filtered (0.45 μ) as soon as possible. The determination is by the differential cathode ray polarography of bismuth - NTA samples at pH 2.0 as described by Traversy (1971).

Phosphorus

Total phosphorus was determined according to Technicon Industrial Method No. 116-71W. This is an automated method whereby samples are digested onstream by a Technicon Continuous Digester followed by determination of the orthophosphate. Orthophosphate is reacted with ammonium molybdate in acid solution and the complex is subsequently reduced with amino-naphthol sulfonic acid to give molybdenum blue which is measured colourimetrically.

Total Kjeldahl Nitrogen (TKN)

TKN was determined according to Technicon Industrial Method No. 146-71A. This also involves continuous sample digestion with a Technicon

Continuous Digester, followed by determination of liberated ammonia by the Berthelot reaction.

Nitrate/Nitrite

Nitrate and nitrite were determined according to Technicon Industrial Method No. 100-70W by an automated procedure. Nitrite ion reacts with sulfanilimide under acidic conditions to form a diazo compound. This compound reacts with N-1-naphthylethylenediamine dihydrochloride to form a reddish-purple azo dye which is measured colourimetrically. Nitrate is reduced in a copper-cadmium column to nitrite and is determined by difference.

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Utilization of industrial wastes and waste by-products for phosphorus removal : an inventory and assessment /
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